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A Memoir on the Raman Effect in Liquids

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(Plates VI to IX)

Abstract.

The paper describes the results of a study of the Raman spectra of a large number of compounds suitably chosen so as to be representative of well defined chemical types.

All the hydrocarbons of the paraffin series show a prominent band corresponding to shifts of about 2850-2960 ; the band is distinctly resolved into five components more or less equally spaced, the relation of the constant of spacing (which is about 27 wave numbers) to the rotational frequency of the molecule is discussed.

In carbon disulphide there is no correspondence between the molecular frequencies obtained from the Raman spectrum and infra-red absorption measurements.

Among the halogen derivatives of methane, chloroform and bromoform are of special interest. A comparison of the Raman spectra of the two liquids brings out the influence of the mass of the substituents on the positions of the Raman lines.

The structure of Raman band shifted by about 2960 wave numbers appearing in the spectrograms of the alcohols is discussed with special

reference to its development as we proceed up the series. The influence of isomers is conspicuously pointed out in the case of the alcohols.

The origin of the prominent continuous spectrum scattered by glycerine is discussed in detail.

In the case of the fatty acids, there is a general continuous spectrum which is appreciable in butyric acid.

A strong Raman line corresponding to a shift of 1700 wave numbers appears to be characteristic of the carbonyl groups.

All the nitrocompounds give a prominent Raman line shifted by 1347 wave numbers.

The characteristic differences between the aliphatics and aromatics in respect of the radiations near about 3 μ and 10 μ are pointed out. The Raman spectra of the three xylenes are considered in some detail as typical examples of the influence of substitution.

The Raman spectra of diethyl ether and methyl-phenyl ether are discussed.

In cyclohexane we get the Raman lines which are characteristic of both the open chain and cyclic compounds. The band at $\Delta\nu$ 2853-2935 characteristic of the aliphatic compounds is very prominent. Its structure is compared with that present in the paraffins. $\Delta\nu$ 800 which is very prominent appears to be characteristic of this liquid.

The Raman spectra of pyridine and benzene are compared. In addition to the benzene lines we get a few new lines of which the one at $\Delta\nu$ 1027 is the most prominent. Polarisation measurements show that the corresponding Raman lines in the two liquids are polarised to nearly the same extent, indicating the similarity in structure between the two molecules.

Quinoline gives a prominent fluorescent spectrum. Its Raman spectrum shows great similarity to that of naphthalene. $\Delta\nu$ 1370 is the most prominent in the two compounds.

The Raman spectra of sulphuric, hydrochloric and nitric acids are studied. Sulphuric acid gives a continuous spectrum in addition to the lines. Hydrochloric acid shows only the water bands which tend to sharpen as the concentration increases. In nitric acid (65%) many prominent lines appear in addition to the water band which is resolved into three sharp components as in ice.

Solutions of potassium carbonate and sodium carbonate give a prominent Raman line at $\Delta\nu$ 1064 which may be identified with the inactive frequency of CO_3 ion.

The Raman spectra of water and ice have been studied in detail. The well known 3μ band of water really consists of three components, $2{\cdot}77\mu$, $2{\cdot}90\mu$ and $3{\cdot}13\mu$ of which the second is the most prominent. The structure of this band in ice and crystals containing water of crystallisation and in electroytes is discussed. The effect of temperature on this band has also been studied.

The non-correspondence of the molecular frequencies as obtained from the Raman lines and direct infra-red measurements is discussed and explained on the wave mechanical treatment of dispersion.

The Raman lines in the aliphatic hydrocarbons are generally more polarised than those of the aromatics, thus indicating a close analogy to the classical scattering.

Introduction

The recent discovery by Prof. Raman[1] of a remarkable type of secondary radiation produced by light scattering is of fundamental importance and opens out a new field of research in spectroscopy. Apart from the theoretical significance of the discovery, it supplies us with a powerful and accurate method of investigating molecular spectra, especially in the extreme infra-red region which is not accessible to the ordinary spectrometer. Even in the near infra-red the study of absorption spectra involves very difficult experimental technique; and the spectra are often very diffuse extending over several angstroms especially in the case of liquids. On the other hand, the Raman lines are fairly sharp and the corresponding frequencies of the medium can therefore be ascertained with a degree of accuracy comparable with that of spectroscopic investigation in the visible region. Further, by photographing the Raman spectra we get in a single exposure all the

[1] A New Radiation, by C. V. Raman, Ind. Journ. Phy. Vol II, p. 387 (1928). See also C. V. Raman and K. S. Krishnan—Nature. Vol. 121, p. 501, 31st March, 1928 and A New class of spectra due to secondary radiation, Part I, by C. V. Raman and K. S. Krishnan, Ind. Jour. Phy, Vol. II, p. 399 (1928)

infra-red frequencies simultaneously mapped and thus the experimental investigation is extremely simple.

This aspect of the discovery has naturally attracted considerable attention from investigators all over the world. Though a large number of compounds have been studied for their Raman spectra during the last one year, the investigations have been confined to more or less isolated substances or groups, and it was therefore considered desirable to make a systematic study of a large number of compounds, especially with a view to ascertain the influence of their chemical constitution on the Raman Spectra. For this purpose the substances were suitably chosen so as to be sufficiently representative of different well-defined chemical types, both organic and inorganic. The present paper gives a detailed account of the results of these investigations. The usefulness of such investigations on Raman Spectra for a representative collection of compounds, in any attempt to work out a satisfactory theory of the effect need hardly be emphasised.

Experimental.

It is essential that the liquids used for the study of scattering should be absolutely pure and free from dust and flourescent impurities. The effect of these impurities is to produce a continuous spectrum which obliterates the modified lines. Wherever available Kahlbaum's pure liquids were used and in some cases Merck's extra pure chemicals. The liquids were further purified and made dust-free by slow distillation in large double-bulbs of 500 ccs. capacity.

As source of light a quartz mercury vapour lamp (flat type) of 3000 c. p. made by the Hewitt Electric Company was used. With a current of 4 to 5 amperes from a 220 volt main the lamp worked steadily and needed very little attention.

Two arrangements were used for photographing the scattered spectrum. The first was the method used by

Raman[2] and Raman and Krishnan[3] where the liquid was contained in a bulb and illuminated by condensing the light from the mercury arc by means of an 8-inch glass condenser. The spectroscope was placed with the slit almost touching the bulb the axis of the spectroscope being at right angles to the track in the liquid, and so aligned as to "view" the greatest depth of the illuminated track. Though the method was convenient the serious drawback was that the illumination was low and consequently a long exposure was necessary.

The second arrangement was the one described by Wood.[4] The liquid was contained in a glass tube about 10 inches long and 1 to $1\frac{1}{2}$ inches in diameter, drawn out at the farther end into a horn which was painted black on the outside so as to furnish a dark back ground. To the observation end was cemented a plane glass window. This tube was fitted with a water jacket and the liquid was illuminated with the mercury arc placed almost touching it through its length. The outer wall of the jacket on the side away from the arc was silvered so as to send back the light into the liquid. The illumination obtained by this arrangement was very great. The Raman lines in many cases could be seen visually with great ease. The illuminated liquid column was focussed on to the slit of the spectroscope with a Zeiss lens of 7 cm. focal length. The axis of the spectroscope was placed in a line with the axis of the liquid tube.

Two spectrographs were chiefly employed in the course of the investigation. The E_2 quartz spectrograph of Adam Hilger giving a dispersion of 36 A. U. per m.m. at λ 4000 and a large 2-glass prism spectrograph of great light gathering power, also made by Adam Hilger and giving a dispersion of 20 A. U. per m.m. at λ 4000.

[2] *loc. cit.*
[3] *loc. cit.*
[4] R. W. Wood. Phil. Mag, Vol VI, p. 729 (1928).

For photographing the spectra Ilford Iso-zenith plates, speed H and D 700 were used. These were backed before use to eliminate the halation accompanying the strong lines. For the longer wave-length visible region backed panchromatic plates 2000 speed were found to be most suitable.

Filters :—In general the complete spectrum of the mercury arc was used as the incident radiation. On the quarter plate the spectrum covered the region comprising the wave lengths from λ 3300 to λ 7000. But in some cases where the liquid was highly fluorescent or was acted upon by ultra-violet rays it was found necessary to use filters so as to admit only particular regions of the spectrum. The following list gives the various filters employed and the regions transmitted by them.

(*a*) Corning glass G 586 :—This filter is completely opaque to the visible regions of the spectrum, transmitting only a narrow region of the mercury spectrum in the ultra-violet including the λ 3650·1 A.U. group.

(*b*) Zeiss Blue glass :—This cuts out all the visible lines of wave-length longer than λ 4358·3 A.U. but is transparent to the other regions of the mercury spectrum.

(*c*) Strong solution of quinine sulphate followed by the Zeiss Blue glass filter :—Only the λ 4358·3 A.U. group of lines is transmitted through this combination of filters.

(*d*) Potassium chromate solution :—In suitable concentration it is opaque to violet and ultra-violet regions and transmits only the λ4358·3 A.U. group and lines of longer wave-lengths.

Wave-length measurements :—The plates were measured on a Hilger Cross Slide photomeasuring micrometer reading to a thousandth of a millimeter. For comparison either the spectrum of the iron arc or that of the copper arc was used. In some plates the incident mercury lines themselves were taken as standards. The wave-lengths were calculated using the well-known Hartmann's dispersion formula.

Results.

In the following pages the Raman spectra of a number of compounds are discussed. Under each of the groups of compounds are given the values of the shifts in wave-numbers between the exciting line and the Raman lines and the corresponding wave-lengths in $\lambda_{Ra}\mu$ units are tabulated along with the values obtained in μ from direct infra-red measurements. With the exception of phenyl-methyl ether, cyclo-hexane and the inorganic acids the infra-red absorption values given in the Tables are from Coblentz's " Investigations on Infra-red Spectra." For the first two liquids the data have been taken from J. Lecomte's " Le Spectra Infra-rouge " and for the inorganic acids Pfund's values obtained from the measurements on the reflection maxima are given. The intensities of the Infra-red values are represented by abbreviations in the brackets. In the series of Tables shown at the end of the paper are given the wave-numbers of the Raman lines in the liquids studied, their origin and their relative intensities. For those Raman lines which coincide with the incident lines of the mercury spectrum the measurements are not given in these Tables.

Under each group of compounds the series relationships have been shown and the influence of homology, substitution, isomerism and chemical bonds are discussed in detail.

1. *Paraffins.*

Three members of the paraffin series were investigated, *viz.*, pentane, heptane and octane, and the results are tabulated in Table I. The most prominent feature in the Raman Spectra of these liquids is the band corresponding to a shift of about 2850-2960 wave numbers. On close examination this band is distinctly resolved into five lines of more or less the same intensity, and regularly spaced, the constant of

spacing being about 27 wave-numbers. It is extremely fascinating to speculate on the origin of this regular spacing in the band structure and from the order of magnitude of the constant one is tempted to attribute it to the *rotational* frequency of the molecules. In that case one would have expected a diminution in spacing as we go up the series which would be very rapid if the rotation is about an axis perpendicular to the length of the carbon chain, and a relatively smaller diminution if the rotation is about the long axis of the molecules. The experimental results given in Table I definitely exclude the possibility of the first alternative but however are not sufficiently precise to give any information regarding the second. It would be of great interest, therefore, to study the Raman Spectra over a much wider range in the series, and especially earlier members, *e.g.*, methane, ethane etc., and the authors propose to take up the work shortly. Also, if the idea is correct we should expect a large diminution in the spacing as we pass from the normal paraffins to their different isomers and experiments are in progress to test this point.

Coming to the other Raman lines in the series we find that those corresponding to shifts in wave-numbers of 401 and 769 diminish rapidly in intensity as we go up the series, and this fact is also in accordance with the direct infra-red observations of Coblentz. There is also a small continuous spectrum which is specially noticeable in octane. The intensity of this continuous spectrum increases as we go up the series.

An observation of some interest in connection with octane may be mentioned here. On exposure to the light of the mercury arc even the most carefully purified liquid shows a strong tendency to develop a pink colour. The colour gradually fades away if the liquid is allowed to remain in the dark for a sufficiently long time. As far as we are aware there does not appear to be any isomer of octane which exhibits colouration.

Paraffin Series.

TABLE I.*

Pentane			Heptane			Octane		
$\Delta\nu$	λ_{Ra}	$\lambda_{i.r}$	$\Delta\nu$	λ_{Ra}	λ_{ir}	$\Delta\nu$	λ_{Ra}	λ_{ir}
143	69·9 (2)	...	147	68·0 (1)	...	156	64·1 (0)	...
279	35·8 (0)	...	274	36·5 (0)	...	282	35·5 (0)	...
			312	32·0 (1)	...	336	29·8 (0)	...
346	28·9 (0)	...	346	28·9 (1)	...	352	28·4 (2)	...
401	24·4 (2)	...	407	24·6 (1)	...	...	...	...
			447	22·4 (1)	...	...	...	...
476	21·0 (1)	...	499	20·0 (0)	...	...	...	...
			546	18·32 (1)	...	...	...	...
			720	13·89 (0)	...	...	...	13·8 (s)
766	13·05 (1)	...	769	13·00 (3)	...	...	...	13·3 (f)
839	11·92 (1)	...	...	...	...	814	12·3 (0)	12·3 (f)
869	11·51 (0)	...	845	11·83 (2)	...	861	11·61 (0)	...
905	11·05 (0)	...	903	11·07 (2)	...	896	11·16 (1)	11·3 (f)
964	10·37 (0)	...	967	10·34 (2)	...	964	10·35 (1)	10·43 (m)
1032	9·69 (1)	...	1034	9·67 (2)	...	1033	9·68 (0)	...
1072	9·28 (1)	...	1088	9·19 (1)	...	1079	9·27 (0)	9·32 (f)
		...	1132	8·83 (0)	...	1139	8·78 (1)	...

* In the tables that follow the abbreviations given below are used.
λ_{Ra} = wave length of the Raman lines in μ

$\lambda_{i.r}$ = wave length of infra red absorption lines in μ

Infra red lines :—s = strong, *m* = medium, *f* = faint.
Raman lines :—s = sharp, *b* = broad, *v.b* = very broad, *d* = diffuse, *dr* = diffuse towards red, *dv* = diffuse towards violet.

TABLE I—*contd.*

	Petnane	Heptane				Octane		
$\Delta\nu$	λ_{Ra}	$\lambda_{i.r}$	$\Delta\nu$	λ_{Ra}	λ_{ir}	$\Delta\nu$	λ_{Ra}	λ_{ir}
1163	8·60 (1)		1162	8·61 (1)	...	1155	8·66 (0)	8·62 (m)
			1244	8·04 (1)	...	...	...	...
			1266	7·90 (1)	...	1268	7·89 (0)	7·8 (m)
1303	7·67 (1)	...	1304	7·67 (2)	...	1300	7·69 (2)	
						1338	7·47 (1)	...
1358	7·36 (0)	...	1348	7·42 (2)	...	1356	7·37 (1)	7·33 (s)
1403	7·13 (1)	...	1400	7·14 (1)	...	1398	7·15 (1)	...
1461	6·84 (4)	...	1453	6·88 (3)	...	1447	6·91 (2)	6·87 (s)
						...	...	6·2 (f)
						...	...	5·82 (m)
						...	...	4·0 (f)
2854	3·50 (2)	...	2853	3·51 (4)	...	2851	3·51 (3)	...
2876	3·48 (4)	...	2872	3·48 (3)	...	2873	3·48 (2)	...
2906	3·44 (2)	...	2912	3·43 (3)	...	2907	3·44 (1)	3·43 (s)
2937	3·40 (3)	...	2931	3·41 (4)	...	2936	3·41 (3)	...
2964	3·37 (3)	...	2963	3·38 (3)	...	2964	3·37 (3)	...

ii. *Halogen Derivatives af Methane.*

We next take up some simple halogen derivatives of methane. These substances are characterised by the appearance in their Raman Spectra of only a few lines which are, however, much more intense than those appearing in the Raman Spectra of the paraffins. The fewer number is evidently due to their simple structure.

One striking fact in the Raman spectrum of carbon tetrachloride is the absence of shifts corresponding to about 3μ which appears in the spectra of all organic liquids ; and one can therefore safely attribute the appearance of the lines or bands in the neighbourhood of 3μ to the presence of hydrogen. This is confirmed by the fact that when one of the chlorine atoms in carbon tetrachloride is replaced with hydrogen the 3μ line makes its appearance.

The Raman spectra of chloroform and bromoform show a striking similarity, only the shifts of the various Raman lines from the exciting line are smaller in the case of bromoform than in chloroform, presumably due to the relatively greater mass of Br. The 3μ Raman line is naturally in the same position in the spectra of the two substances.

Whereas all the Raman lines in carbon-tetrachloride, chloroform, and bromoform are fairly sharp there is one line in the spectra of each of these substances which is very diffuse. This line corresponds to a shift of 762-791 for carbon-tetra-chloride, 762 for chloroform and 657 for bromoform. Evidently these molecular frequencies have a similar origin.

In the Raman spectrum of carbon tetrachloride there is a feeble diffuse line corresponding to a shift in wave number of 1535 which is exactly double that of 762-791 and may therefore be a harmonic of the latter frequency.

TABLE II.

Chloroform.			Bromoform			Carbon tetrachloride		
$\Delta\nu$	λ_{Ra}	$\lambda_{i.r}$	$\Delta\nu$	λ_{Ra}	$\lambda_{i.r}$	$\Delta\nu$	λ_{Ra}	$\lambda_{i.r}$
			154	64·94 (3)				
			223	44·84 (3)		216	46·29 (5)	
261	38·31 (5)							
						313	31·95 (7)	
367	27·25 (6)							
						459	21·79 (8)	
			540	18·52 (2)				
			657	15·22 (2)				
669	14·95 (6)							
762	13·12 (3)					762	13·12 (2)	13·6-12·3 (s) Broad
						791	12·64 (2)	
		11·8 (s)						
		10·82 (s)						
		10·2 (f)						10·1 (m)
		9·6 (s)						
								9·0 (m)
1218	8·21 (2)	8·3 (s)						8·25 (m)
								8·02 (m)
		7·2 (s)						
1441	6·94 (1)	6·8 (s)						
						1535	6·51 (0)	6·45-6·57 (s)
		5·9 (f)						5·8 (f)
		5·6 (f)						
		4·4 (f)						
		3·8 (f)						
3019	3·31 (4)	3·32 (m)	3020	3·31 (0)				
		2·75 (f)						

iii. *Carbon disulphide.*

The case of Carbon disulphide is of exceptional interest in view of the fact that there is no correspondence between the molecular frequencies given by the various Raman lines and those appearing in infra-red absorption. In this respect it has a strong resemblance to the case of Carbondioxide which has recently been studied by Rasseti[6] in the gaseous state. This is probably to be expected in view of the close similarity in the structure of the two molecules. For example Carbon disulphide shows very strong infra-red absorption bands at 13·4 μ, 11·65 μ, 6·5 μ and 4·6 μ which have no corresponding Raman lines at all, while again the two Raman frequencies $\triangle\nu$ 655 and $\triangle\nu$ 800 have no corresponding infra-red bands. The case of Carbon disulphide is not exceptional in this respect since the lack of exact parallelism is more or less of general occurrence. Only Carbon disulphide offers an exceptionally striking example. This question shall be discussed in detail in a later section when all the experimental data have been tabulated.

It is interesting to note that modified lines generated by the mercury line λ 5460 and *even by the weak green line* λ 4916 appear in the spectrogram of this liquid.

TABLE III.

Carbon disulphide.

$\triangle\nu$	655		800				
λ_{Hg}	15·27 (10)		12·50 (3)				
$\lambda_{i.r}$		13·4 (s)		11·65 (s)	6·8 (s)	4·6 (s)	3·2 (m)

[6] Rassetti. Nature Vol. 123, p. 205, Feb. 9, 1929.

iv. *Alcohols.*

The prominent feature in the Raman spectra of monohydric alcohols is the band corresponding to a shift of about 3·5 μ to 3·4 μ. The variation in the structure of this band as we go up the series is extremely interesting. In the first member, *viz.*, methyl alcohol it ceases to be a band but consists of two more or less sharp well defined lines of the same intensity, their shifts from the exciting lines being 2834 and 2939 wave numbers respectively. On the other hand when we go to ethyl alcohol it can be clearly recognised as three well defined lines corresponding to shifts of 2872, 2930, and 2973 wave numbers, the central Raman line being brighter than the lines on either side. In the case of propyl alcohol it consists of four lines having shifts of 2873, 2913, 2945, and 2970 wave numbers, the intensity of the line corresponding to the first shift being the greatest and falling off as we go to longer shifts. There is also a very marked continuous spectrum noticeable between the lines. The band in isopropyl alcohol also shows a similar structure the four components being in practically the same positions as in *n.* propyl alcohol; however their relative intensities are slightly altered, the line corresponding to the longest shift, *viz.*, 2976 being the most intense, the one having the smallest (2879) coming next in order, the other two lines being of the same intensity and coming last.

As we proceed still higher up the series, the continuous spectrum between the two extreme lines of the band becomes so conspicuous that in the case of iso-butyl alcohol one can detect a structure inside only with great difficulty, while in the case of isoamyl alcohol (inactive) the continuous spectrum is quite homogeneous.

Regarding the other lines in the spectra of the alcohols we may mention in the first place that fresh lines begin to

appear as we proceed up the series, especially on the shorter wave-length side ((*i.e.*,) corresponding to shorter shifts from the exciting line). This is probably to be expected from the increasing complexity and mass of the molecule as we go up the series. In connection with the question of the influence of the complexity of the molecule on its Raman lines attention may also be drawn to the striking contrast between the normal alcohols and their isomers. Whole groups of fresh Raman lines appear in the spectrum of the isomers which are not present in the spectra of the corresponding normal alcohols.

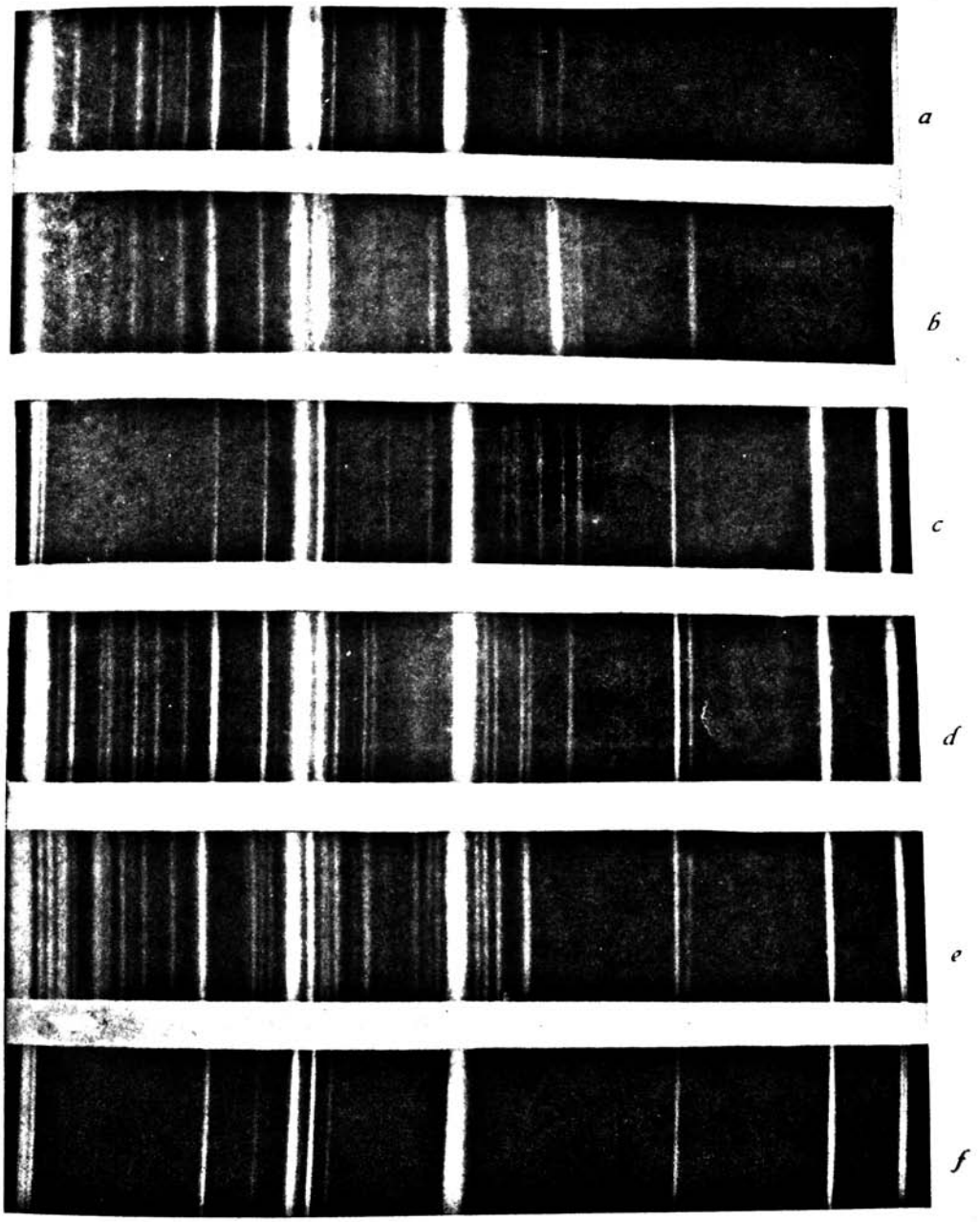
The prominent Raman line corresponding to a shift of about 1460 wave numbers appears to be a characteristic of all the alcohols. It appears also as a very strong line in the spectrum of glycerine and in a slightly shifted position in the spectrum of phenol.

The general continuous back ground extending over a large range, which accompanies the Raman lines also increases as we go up the series. While it is practically absent in the earliest members it first becomes appreciable with propyl alcohol and is very conspicuous in the spectrum of amyl alcohol.

The Raman lines of allyl alcohol show a peculiar tendency to group into doublets having more or less the same separation *e.g.*, those corresponding to shifts of 496 and 551, 1105 and 1155, 1289 and 1329, and 1419 and 1468; the components of the doublets are also of about the same intensity. Whether this doublet formation is due to the unsaturated nature (*i.e.*, consequent on its having a double bond) it is difficult to say since allyl alcohol is the only unsaturated alcohol in our list.

In the Raman spectrum of methyl alcohol there is a broad diffuse band extending from λ 4150 to λ 4190. The higher alcohols, *viz.*, propyl, *etc.*, do not show this band, while ethyl alcohol shows a very feeble band in this position. Water which may be regarded as the first member of the

series of monohydric alcohols shows this band very prominently and thus the appearance of this band also in methyl alcohol (which comes intermediate between water and ethyl alcohol in the series) is understandable. We are therefore tempted by analogy with the case of water (See later section) to consider the band λ4150—4190 of methyl alcohol as the Raman band excited by λ 3650 of the mercury arc, which would then correspond to an infra-red wave-length of about 3 μ. If this is the origin of the band we should expect the other prominent lines of the mercury arc, *viz.*, λ 4046 and λ 4358 also to excite corresponding Raman bands (which in fact appear in the spectrum of water), but the spectrogram of methyl alcohol does not show the existence of any such bands. The only explanation of this difficulty that suggests itself is that the intensity of this Raman band excited by different incident lines falls off very rapidly as the wave length of the exciting line increases—in fact very much more rapidly than is generally the case for the Raman lines. Why this particular Raman radiation should behave anomalously in this respect is a matter for further consideration. An extended study of methyl alcohol especially in the ultra-violet region would therefore be of interest.



(a) nitric acid, (b) amyl alcohol, (c) nitromethane,
(d) chloroform, (e) carbon tetrachloride, (f) Hg spectrum.

Alcohols.

TABLE IV.

Methyl alcohol.			Ethyl alcohol.			Propyl alcohol.		
$\Delta\nu$.	$\lambda_{Ra.}$	$\lambda_{i.r.}$	$\Delta\nu$.	$\lambda_{Ra.}$	$\lambda_{i.r.}$	$\Delta\nu$.	$\lambda_{Ra.}$	$\lambda_{i.r.}$
...	...	...	450	22·2(0)	...	454	22·0(0)	...
...	...	13·2(*f*)	...	...	...	...	...	13·0(*m*)
...	...	12·5(*f*)	...	...	...	...	...	...
...	...	11·5(*f*)	884	11·31(3)	11·4(*s*)	864	11·57(0)	11·2(*m*)
...	...	...	...	...	...	970	10·31(1)	10·4(*s*)
1081	9·70(2)	9·9(*s*)	1047	9·55(1)	9·6(*s*)	1063	9·41(0)	9·5(*s*)
...	...	9·0(*m*)	1165	8·58(0)	...	...	...	...
1257	7·96(1)	8·2(*m*)	1272	7·86(1)	7·8-7·0 (*s*)	1288	7·76(0)	...
1360	7·35(2)	...	...	...	very broad	136	7·33(0)	7·2(*s*)
...		7·0(*s*)						
1465	6·82(1)	...	1461	6·84(2)	...	1464	6·83(2)	6·9(*s*)
...	...	...	...	...	6·2(*f*)	...	...	6·1(*f*)
2884	3·53(8)	...	2872	3·48(2)	3·44(*s*) broad	2873	3·48(4)	3·5(*s*)
						2913	3·43(8)	...
2939	3·40(3)	...	2930	3·41(4)		2945	3·40(3)	...
...	...	...	2973	3·36(2)	...	2970	3·37(1)	...
...	...	3·0(*s*)	...	...	...	...	...	3·0(*s*)

TABLE V

Isopropyl alcohol			Isobutyl alcohol			Isomyl Propul		
Δ_ν	λ_{Ra}	$\lambda_{i.r}$	Δ_ν	λ_{Ra}	$\lambda_{i.r}$	Δ_ν	λ_{Ra}	$\lambda_{i.r}$
155	64·5 (0)		150	66·7 (1)				
310	32·3 (0)					220	45·4 (0)	
372	26·9 (0)		394	25·4 (1)		341	29·3 (0)	
438	23·1 (1)					450	22·2 (0)	
488	20·5 (1)		495	20·20(2)				
736	13·59 (0)	13·5 (*m*)			13·3 (*m*)	520	19·2 (0)	13·3 (*f*)
761	13·14 (0)	13·0 (*m*)	789	12·67 (1)	12·7 (*f*)	767	13·03 (2)	13·0 (*f*)
820	12·20 (6)	12·2 (*s*)	819	12·21 (5)	12·2 (*m*)	830	12·04 (2)	12·0 (*f*)
			910	10·99 (0)	11·0 (*f*)	894	11·19 (0)	11·0 (*f*)
					10·6 (*f*)			
955	10·47 (3)	10·5 (*s*)	962	10·40 (1)	10·4 (*m*)	955	10·47 (1)	10·3 (*f*)
1008	9·92 (1)					1011	9·88 (1)	9·9 (*s*)
1053	9·50 (0)		1049	9·53 (0)	9·6 (*s*)	1055	9·49 (0)	9·5 (*s*)
		9·0 (*s*)					-	
1143	8·75 (1)	8·6 (*s*)	1129	88·6 (0)		1123	8·90 (0)	8·9 (*f*)
						1168	8·56 (0)	
		7·6 (*s*)	1251	7·99 (1)	8·1 (*m*)	1286	7·77 (0)?	8·2 (*f*)
1340	7·46 (0)	7·3 (*s*)	1342	7·45 (1)	7·2 (*s*)	1339	7·47 (1)	7·3 (*s*)
1454	6·88 (3)	6·9 (*s*)	1462	6·84 (3)	6·9 (*s*)	1458	6·86 (4)	6·9 (*s*)
		5·9 (*m*)			6·2 (*f*)			
						1656	6·04 (0)?	5·4 (*f*)
2665	3·75 (0)		2665	3·75 (0)				
2726	3·67 (0)		2726	3·67 (0)				
2879	3·47 (4)	3·5 (*s*)	2874	3·48 (5)		2880	3·47 (4)	
2919	3·43 (2)							
2938	3·40 (2)							
2976	3·36 (6)		2965	3·37 (5)	3·4 (*s*)	2982	3·35 (5)	3·4 (*s*)
		3·0 (*s*)			3·0 (*s*)			3·0 (*s*)

TABLE VI

Allyl alcohol			Phenol			Glycerine		
$\Delta\nu$	λ_{Ra}	$\lambda_{i.r}$	$\Delta\nu$	λ_{Ra}	$\lambda_{i.r}$	$\Delta\nu$	λ_{Ra}	$\lambda_{i.r}$
291	34·4 (0)							
361	27·7 (0)							
437	22·9 (2)							
496	20·2 (0)					485	20·61 (5)	
551	18·1 (1)							
			616	16·23 (0)				
642	15·6 (0)					679	14·72 (0)	
		13·5 (*m*)						13·8 (*f*)
754	13·26 (0)	13·2 (*f*)	763	13·11 (0)				
		11·7 (*f*)	818	12·22 (1)		841	11·89 (1)	11·8 (*m*)
911	10·97 (2)	10·9 (*s*)				923	10·84 (1)	10·9 (*s*)
997	10·03 (2)	10·0 (*s*)	1007	9·93 (2)				
1031	9·70 (1)							
								9·1 } (*s*) 9·6 }
1105	9·05 (2)	9·0 (*s*)				1080	9·26 (4)	
1155	8·66 (1)	8·3 (*m*)	1178	8·49 (0)				
								8·2 to 7 } (*s*)
1289	7·76 (3)							
1329	7·52 (2)	7·5 (*f*)						
			1363	7·34 (0)				
1419	7·05 (2)	7·0 (*s*)						
1468	6·81 (2)		1495	6·69 (0)	6·75(*s*)	1466	6·82 (3)	
			1604	6·23 (0)	6·23(*s*)			
1649	6·06 (4)	6.1 (*f*)						5·9 (*m*)
								4·3 (*f*)
2868	3·49 (2)							
2928	3·42 (2)							
						2920	3·43 (4)	3·3 (*s*)
3014	3·32 (3)							
		3·2 } (*s*)						
3079	3·25 (1)	3·0 }	3060	3·27 (3)				
	?							
			3383	2·96 (0)?	2·97(*s*)			

Glycerine.

This liquid has already been investigated by one of us[6] in detail and it shows in addition to the usual Raman lines a continuous spectrum which is exceptionally strong. A repeated

[6] S. Venkateswaran, Ind. Jour. Phy. Vol. II, p. 105 (1928).

purification of the liquid does not seem to diminish the intensity of the continuous spectrum. Also different specimens (*e.g.*) Kahlbaum's, Mercks' Extra pure, and Mercks' Reagent specially fractionated to 100 per cent. in high vacuum show practically the same intensity. We should therefore conclude that the continuous radiation is as much a characteristic of glycerine as its Raman lines.

That the intensity of the continuous spectrum is intimately connected with its very large viscosity has been definitely shown in the paper referred to. For a given mass of glycerine the intensity falls off rapidly as its viscosity is diminished, (*e.g.*), by heating or by diluting it with water.

From a study of the distribution of intensity of the continuous spectrum excited by individual mercury lines of various wave-lengths (*e.g.*, λ3650, λ4046, λ4358) we find that the intensity extends over a large range which does not differ considerably for the different exciting lines. At first sight it seems to suggest that the continuous radiation may be of the type of fluorescence—which is, however of an entirely different order of intensity.

It must be pointed out in this connection that the appearance of the continuous spectrum is not peculiar to glycerine. Almost every substance, even in the most carefully purified state radiates a small continuous spectrum. Only glycerine exhibits it to a remarkable extent, and any explanation of the continuous spectrum of glycerine should therefore be capable of explaining it in other liquids also. That all liquids should exhibit fluorescence in very nearly the same visual region of the spectrum is very difficult to understand.

Indeed, the observed fact that the continuous radiation from a non-viscous (at least relatively to glycerine) liquid like amyl alcohol is even more strongly polarised than the continuous radiation from glycerine, seems to present a difficulty in accepting the idea of fluorescence. We are therefore inclined to treat it as a type of Raman radiation. A detailed

study of the distribution of intensity in the continuous spectrum excited by various wave-lengths would be necessary to confirm this conclusion. A study of the polarisation of the continuous spectrum scattered by glycerine at various degrees of dilution with a non-viscous liquid like water may throw light on the question.

V. The Fatty Acids.

The Raman spectra of the fatty acids show a general resemblance to the Raman spectra of the corresponding monohydric alcohols, *e.g.*, butyric acid and propyl alcohol, propionic acid and ethyl alcohol, etc. The band at 3·4 μ characteristic of the alcohol series also appears in the spectra of the fatty acids and as in the former shows a tendency to broaden as we go up the series. In the case of butyric acid the components of the band are so diffuse that it is only with some difficulty that any structure can be detected, though in acetic acid the band can be easily seen to be resolved into three lines, the central line being sharp and the most intense and those on either side of it being more diffuse.

Indeed, it may be stated as a general fact of observation that all the Raman lines of fatty acids are more or less diffuse (in comparison with the Raman lines of other liquids), the diffuseness of the lines increasing as we go up the series.

The diffuse line corresponding to 16·0 μ which is fairly intense in acetic acid tends to fade away as we go to propionic and butyric acids.

The general continuous radiation which is present only to a small extent in acetic and propionic acids becomes appreciable in butyric acid.

TABLE VII.

Fatty acids.

Formic acid.		Acetic acid.		Propionic acid.		Butyric acid.	
$\Delta\nu$	λ_{Ra}	$\Delta\nu$	λ_{Ra}	$\Delta\nu$	λ_{Ra}	$\Delta\nu$	λ_{Ra}
196	51·0 (1)	...	...	...	...	...	...
...	...	283	35·3 (0)	...	...	269	37·2 (0)
...	...	362	27·6 (1)	...	...	...	...
449	22·3 (0)	446	22·4 (1)	...	...	462	21·6 (1)
...	...	...	...	485	20·6 (0)	...	...
...	...	623	16·0 (3)	608	16·4 (0)	613	16·3 (1)
690	14·5 (1)	...	...	...	...	...	...
...	...	766	13·1 (0)	770	12·98 (1)	778	12·85 (1)
857	11·7 (0)	...	...	854	11·71 (5)	869	11·50 (1)
...	...	901	11·10 (5)	...	...	...	...
...	...	946	10·56 (0)	...	...	...	...
...	...	978	10·22 (0)	...	...	...	...
1052	9·51 (0)	1021	9·79 (0)	1033	9·68 (0)	1044	9·58 (0)
...	...	...	...	1082	9·24 (1)	...	...
...	...	1128	8·87 (0)	1134	8·82 (0)	1125	8·88 (2)
1223	8·18 (0)	...	...	...	...	...	...
...	...	1280	7·81 (2)	1275	7·84 (1)	1293	7·73 (0)
...	...	1364	7·33 (2)	1365	7·33 (0)	1364	7·33 (1)
1400	7·14 (3)	1433	6·98 (3)[a]	1426	7·01 (4)	1416	7·06 (1)
...	...	...	...	1460	6·85 (3)	1455	6·87 (4)
1694	5·90 (2)	1670	5·99 (0)	1662	6·02 (1)	1659	6·02 (1)
2957	3·38 (4)	2944	3·396 (5)	2955	3·384 (3)	2941	3·399 (2)

Fatty acids (Infra- red absorption values.)

Acetic acid :—Coblentz	3·45 (s)	3·75* (f)	5·86 (s)	7·2 (s)		8·15 (s)	9·6* (f)	9·9 (s)	10·7 (s)	11·5 (s)		13·9* (f)
Butyric acid :—Weniger	3·6 (s)		5·9 (s)	7·1 (s)	7·9 (s)		9·3 (m)		10·6* (s)		12·9 (f)	

VI. Ketones.

The following ketones have been studied (1) Dimethyl ketone, (2) Methyl ethyl ketone, (3) Diethyl ketone, (4) methyl propyl ketone and (5) Acetophenone. The Raman band at 3·4 μ, which has been observed in all the aliphatic hydrocarbons discussed in the previous pages also appears prominently in the ketones, the band also showing a distinct structure in simpler members and broadening rapidly as the molecules become more and more complex. Some of the longest shifts in wave numbers obtained so far are given in these liquids.

There is also a Raman line corresponding to a shift of about 1700 wave numbers (infra-red wave length 5·92 μ) which appears without exception in all the ketones and in the fatty acids and seems to be a characteristic of the carbonyl group. The same wave length also appears conspicuously in the infra-red absorption of liquids containing the carbonyl group.[7]

* no corresponding Raman lines.

[7] See for example J. W. Ellis. Jour. Amer. Chem. Soc. Vol. 51, p. 1384 (1929).

TABLE VIII.

Ketones.

Dimethyl Ketone.			Methyl-ethyl Ketone.			Methyl-propyl Ketone.		
$\Delta\nu$	λ_{Ra}	λ_{ir}	$\Delta\nu$	λ_{Ra}	λ_{ir}	$\Delta\nu$	λ_{Ra}	λ_{ir}
360	27·8 (0)							
			408	24·5 (2)				
544	18·4 (1)		560	17·9 (2)				
		13·1 (*m*)			13·5 (*m*)	591	16·9 (0)	
795	12·58 (5)	12·6 (*m*)	766	13·05 (4)		714	14·0 (6)	
		11·3 (*s*)			10·8 (*m*)			
940	10·64 (0)	10·9 (*s*)	964	10·37 (1)				
		10·4 (*f*)						
		9·7 (*m*)			9·6 (*f*)	1042	9·59 (0)	
1093	9·15 (0)	9·1 (*m*)	1093	9·15 (1)				
			1176	8·50 (0)	8·5 (*m*)			
			1207	8·29 (0)				
1231	8·12 (2)	8·3 (*s*)	1254	7·97 (0)				
1365	7·33 (0)	Broad band	1375	7·27 (1)	7·3 (*s*)			
1433	6·98 (2)	7·6 to 6·6 (*s*)	1431	6·99 (3)	7·0 (*s*)	1446	6·91 (1)	
1718	5·82 (2)	5·75 (*s*)	1729	5·78 (2)	5·9 (*s*)	1718	5·82 (1)	
		4·72 (*m*)			4·9 (*f*)			
2857	3·50 (1)		2876	3·48 (2)	3·6 (*s*)	2866	3·49 (3)	
2928	3·42 (8)	3·42 (*s*)	2926	3·42 (4)		2913	3·43 (5)	
3037	3·29 (1)							
3121	3·20 (1)							
3342	2·99 (0)							
3663	2·73 (1)		3651	2·74 (1)				
3735	2·68 (1)							

TABLE IX

Di-ethyl Ketone.			Acetophenone.			
$\Delta\nu$	λ_{Ra}	λ_{ir}	Δ_ν	λ_{Ra}	λ_{ir}	
			162	61·7 (2)		
406	24·6 (2)					
561	17·8 (1)					
			618	16·18 (1)		
			726	13·77 (2)		
					13·3 (*s*)	
773	12·93 (2)					
					12·2 (*s*)	
					10·9 (*s*)	
988	10·12 (1)		993	10·07 (6)	10·0 (*f*)	
			1017	9·83 (1)		
			1072	9·33 (2)		
1097	9·11 (1)					
			1159	8·63 (2)		
1242	8·05 (1)		1260	7·93 (3)	8·0 (*s*)	
					7·4 (*s*)	
1411	7·09 (1)				7·0 (*s*)	
1469	6·81 (2)					
			1594	6·27 (8)	6·35 (*s*)	
			1679	5·95 (7)	6·05 (*s*)	
1711	5·84 (0)					
2925	3·42 (6)					
			3056	3·27 (3)	3·5 (*s*)	

II. *Nitrocompounds.*

Except nitromethane all the nitrocompounds investigated by us were coloured. Nitrobenzene, ortho nitrotoluene, and para nitrotoluene (the last of which is a solid at ordinary temperatures and was therefore used in our experiments in the form of a solution in carbon tetrachloride) absorb the violet and ultra violet lines of the mercury arc that they do not appear in the spectrogram at all. Meta nitrotoluene and tetra nitromethane cut out even the 4358·3 A. U. group of lines.

In the case of these liquids it is extremely interesting to note that even the green line of mercury λ5461 and in the case of nitrobenzene *even the yellow doublet* give the Raman lines.

The intense Raman line corresponding to a shift of 1347 wave numbers seems to be characteristic of all nitro compounds. The corresponding wave-length also appears conspicuous in infra-red absorption measurements. However, in the case of nitromethane though this Raman line is as intense as in the other nitro compounds investigated, its position is slightly shifted to the longer wave-length side by about 50 wave-numbers. It may be mentioned in this connection that aqueous solutions of sodium nitrite and some nitrates investigated by Carelli, Pringsheim and Rosen [8] (See section on nitric acid) also show the line shifted in the opposite direction by about the same magnitude.

Comparing nitrobenzene and the nitrotoluenes it is found that the substitution of a hydrogen atom with a CH_3 group gives rise to a prominent modified line corresponding to $\Delta\nu$ 2960 which is characteristic of aliphatic compounds. The other lines of nitrobenzene are not altered.

[8] A Carelli, P. Pringsheim and B. Rosen.—Zeits. fur. Physik, Vol. 51, p. 511 (1928).

Nitro Compounds.

TABLE X.

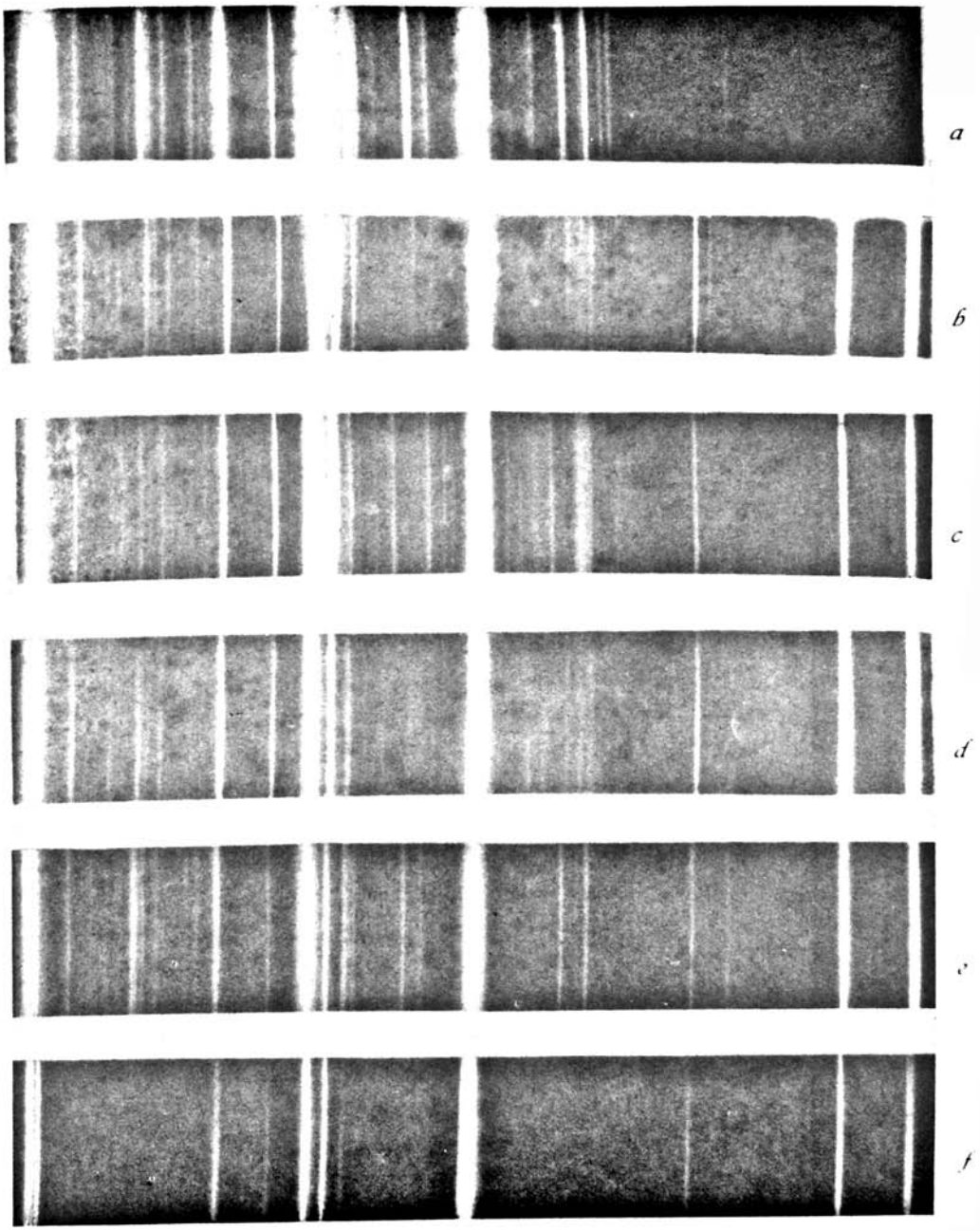
Nitromethane.			Tetranitromethane.			Nitrobenzene.		
$\Delta\nu$	λ_{Ra}	$\lambda_{i.r}$	$\Delta\nu$	λ_{Ra}	$\lambda_{i.r}$	$\Delta\nu$	λ_{Ra}	$\lambda_{i.r}$
485	20·62 (2)							
655	15·27 (3)							14·4 (s)
		13·96 (m)						
		13·2 (f)						12·6 (s)
		12·0 (f)				861	11·61 (1)	11·7 (s)
916	10·92 (6)	10·92 (s)						10·7 (s)
		10·5 (f)						10·0 (f)
		9·95 (f)				1011	9·89 (2)	9·8 (s)
								9·38 (s)
1111	9·00 (1)	9·1 (s)				1116	8·96 (2)	9·07 (s)
		8·7 (f)						8·6 (m)
		8·3 (f)						8·0 (f)
1396	7·16 (6)	7·75 broad to band 6·35 (s)	1331	7.51(1)		1317	7·42 (8)	7·42 (s)
						1530	6·54 (1)	6·6 (s)
1561	6·406 (1)					1589	6·29 (3	6·25 (f)
		5·8 (f)						5·1 (f)
		5·1 (f)						
		4·1 (f)						
2961	3·377 (5)	3·41 (s)						
3042	3·287 (0)					3051	3·278 (0)	3·25 (m)
		2·65 (f)						
		2·58 (f)						
		2·43 (f)						
		2·27 (f)						

TABLE XI.

	Ortho-nitrotoluence.		Meta-nitrotoluene.			Para-nitrotoluene.		
$\Delta\nu$	λ_{Ra}	$\lambda_{i.r}$	$\Delta\nu$	λ_{Ra}	$\lambda_{i.r}$	$\Delta\nu$	λ_{Ra}	$\lambda_{i.r}$
...	...	13·8 (s)	...	...	...	...	...	13·6 (s)
789	12·67 (1)	12·74 (s)	...	...	...	...	...	12·73 (s)
...	...	11·6 (s)	...	...	..	...	...	11·93 (s)
..	...	10·5 (f)	...	...	...	...	..	11·6 (m)
...	...	10·0 (f)	...	...	...	...	...	..
1041	9·61 (2)	9·63 (m)	...	...	...	...	...	9·63 (s)
...	...	9·35 (m)	...	...	...	...	...	...
...	...	8·7 (s)	...	...	...	...	...	9·08 (s)
1189	8·41 (1)	8·38 (m)	...	...	...	...	...	8·65 (f)
								8·3 (m)
1838	7·47 (7)	7·5 (s)	1326	7·45(2)	...	1335	7·49 (4)	7·5 (s)
1474	6·78 (0)	6·86 (s)	...	...	..	...	...	6·86 (s)
...	...	6·6 (s)	...	...	...	...	...	6·6 (s)
1581	6·33 (2)	6·25 (f)	...	...	...	1590	6·29 (0)	6·25 (f)
2953	3·39 (1)	3·43 (m)	...	...	...	...	...	3·43 (m)
3087	3·24 (1)	...	...	...	...	...	...	...
...	...	3·2 (f)	...	...	...	...	...	3·25 (f)

VIII. Benzene and its Derivatives.

We now proceed to the aromatic compounds. Here again we meet with more or less intense Raman lines corresponding to a shift of about 3000 wave numbers, which we have shown to be characteristic of the hydrocarbons. In the aliphatics this Raman radiation appears as a diffuse *band* showing a distinct structure (consisting sometimes of as many as five separate lines), the diffuseness increasing as we go to the higher members, where it appears as a single broad band. The two edges of this band are fairly sharp and correspond to the shifts of 2850 and 2960 wave numbers respectively. On



(a) pyridine, *(b)* ethyl benzene, *(c)* para-xylene,
(d) meta-xylene, *(e)* benzene, *(f)* Hg. spectrum.

the other hand, in benzene this Raman radiation appears as an intense single line whose shift from the exciting line is equal to 3060 wave numbers. This line also appears in the same position in the Raman spectra obtained with all the aromatic compounds. This result is very significant as indicating a distinct structural difference between the aliphatic and aromatic hydrocarbons and thus confirms the general chemical evidence on the subject. That this Raman radiation in benzene should be sharp is probably due to the identity of all the six hydrogen atoms present in the molecule. On the other hand in the aliphatics the hydrogen atoms in the CH_3 groups are presumably different from those appearing in the CH_2 groups; and there may also be differences between the different CH_3 groups themselves in the case of some of the isomers. This would probably explain the diffuseness of the Raman radiation and also account for the distinct structure which it exhibits. When one of the hydrogen atoms in benzene is replaced by an aliphatic hydrocarbon group like CH_3 or C_2H_5 etc. the sharp Raman radiation at $\Delta\nu$ 3060 characteristic of the benzene hydrogens and the diffuse ones at $\Delta\nu$ 2850-2960 characteristic of the aliphatic hydrogens *simultaneously* appear in the spectrogram as we should naturally expect.

There is another equally strong Raman line in the spectrogram of benzene which corresponds to a shift of 990 wave numbers. This line continues to appear in all the benzene derivatives. All the aliphatic compounds also show a characteristic line corresponding to a shift of about 1050 wave numbers, accompanied sometimes by one or two companions in the neighbourhood. The actual value of the shift varies slightly from group to group. If we attribute these frequencies to the oscillation of the carbon atom, the above difference in frequency between the aliphatic and aromatic compounds is easily understood as a necessary consequence of the classical difference between the carbon atoms in the two sets of compounds. The multiplicity of this frequency in the

aliphatics as contrasted with its being single in benzene is probably due to the same cause as we have suggested in the previous paragraph for the corresponding multiplicity of 3·4μ radiation. Here again in the case of benzene derivatives which contain aliphatic carbon groups we get in addition to the Raman line shifted by about $\Delta\nu$ 990 characteristic of the aromatics, also the lines at about $\Delta\nu$1050 due to the aliphatics.

In the case of the benzene derivatives it has been mentioned that apart from the appearance of new Raman lines due to the substituent, the original lines of benzene continue to appear in practically the same *position.* However, their intensities are considerably affected by the substitution. The $\Delta\nu$990 line for example, which is exceptionally strong in benzene is very much weakened in intensity even in such simple derivatives like toluene, while in more complex derivatives it is even feebler. A similar weakening in intensity with substitution can also be observed with the $\Delta\nu$ 3060 line, though to a much smaller extent.

As a typical example of the influence of substitution on the positions and intensities of the Raman lines we will mention here the case of the three xylenes. Most of the Raman lines appearing in their spectrograms are common to the three xylenes; and it is remarkable that the frequencies of these lines remain practically unaffected by the changes in the relative positions of the two CH_3 groups. Some of the lines brighten up conspicuously as we proceed from ortho to meta and from meta to para-xylenes, sometimes new lines appearing in the spectrograms of the latter isomers which are not present in the ortho compound. There are also a few exceptions to this general behaviour, since a few lines appear in the spectrogram of ortho xylene which are not represented in the other two isomers. We may also draw attention to the appearance in all the three cases of frequencies 2869 and 2920 characteristic of aliphatic hydrogen and of 3058 due to the aromatic hydrogen.

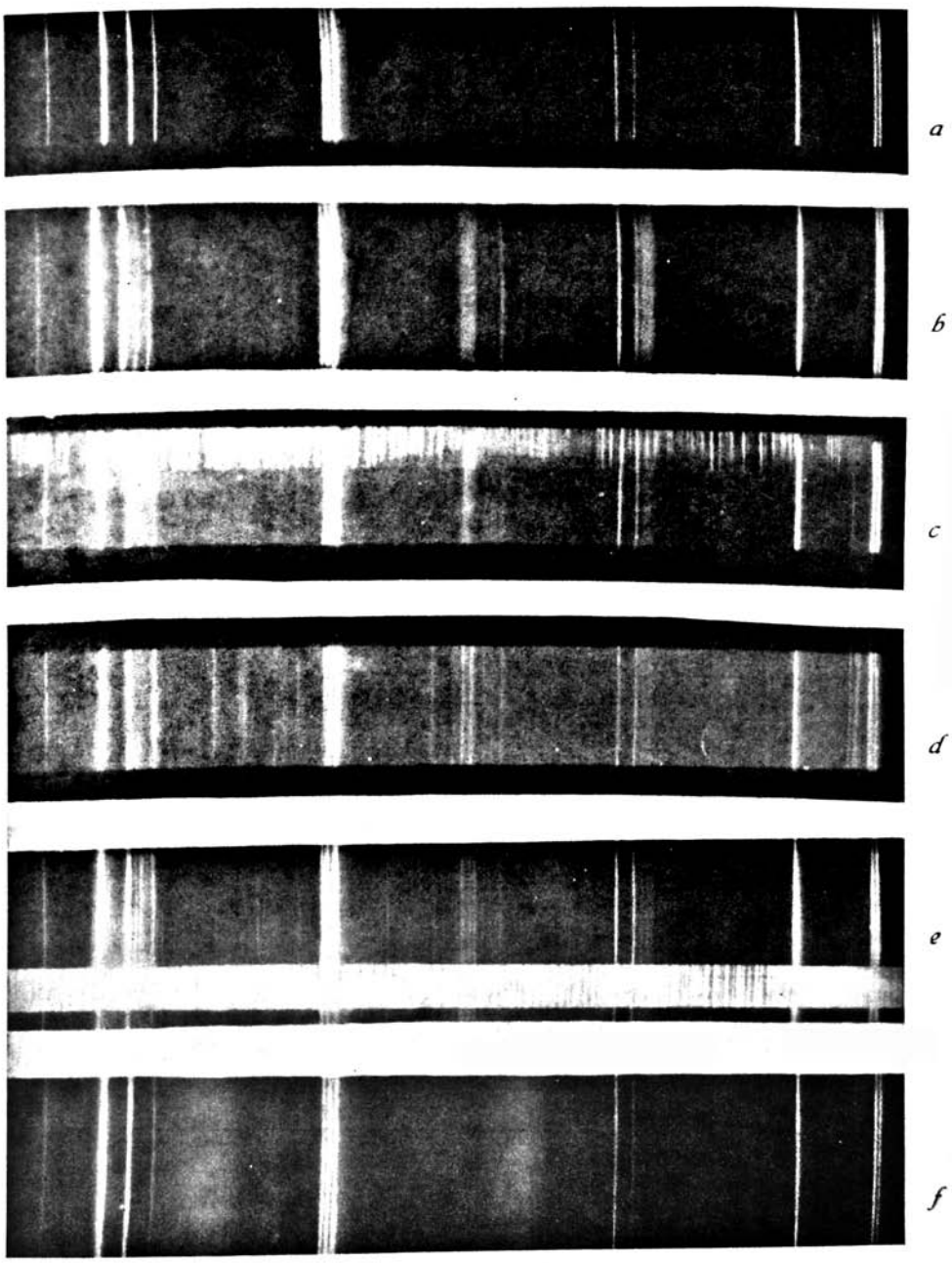
Benzene Series.

TABLE XII.

Benzene.			Toluene.			Ethyl Benzene.		
$\Delta\nu$	λ_{Ra}	$\lambda_{i.r}$	$\Delta\nu$	λ_{Ra}	$\lambda_{i.r}$	$\Delta\nu$	λ_{Ra}	$\lambda_{i.r}$
						153	65·4 (4)	
			215	46·5 (2)				
						305	32·8 (0)	
			345	29·0 (1)				
						399	25·1 (0)	
						447	22·4 (0)	
			520	19·23 (2)		539	18·6 (0)	
605	16·52 (1)		622	16·07 (1)		619	16·16 (0)	
			730	13·69 (0)	13·78 (s)			
		12·95 (s)	786	12·72 (4)	13·0 (f)	770	12·99 (2)	
849	11·78 (0)	11·8 (s)			12·03 (f)			
					11·15 (f)			
					10·6 (f)			
		10·3 } (s)			10·2 (f)	972	10·29 (0)	
991	10·09 (10)	9·78 }	1005	9·94 (7)		1005	9·94 (2)	
			1029	9·71 (1)	9·73 (m)	1031	9·70 (0)	
					9·27 (m)			
1176	8·57 (2)	8·67 (s)	1162	8·60 (1)	8·54 (f)	1153	8·67 (0)	
			1209	8·27 (2)	8·4 (f)	1203	8·31 (2)	
		7·8 (f)			7·7			
		7·25 (f)	1383	7·23 (1)	7·25 (m)			
			1431	6·99 (0)	6·86 } (s)	1456	6·87 (0)	
		6·75 (s)	1503	6·65 (0)	6·7 } (s)			
1592	6·28 (1)	6·2 (f)	1602	6·24 (2)	6·2 (m)	1609	6·22 (0)	
		5·5 (m)			5·5 (f)			
			2921	3·42 (0)	3·34 (s)	2934	3·41 (2)	
3061	3·27 (10)	3·25 (s)	3052	3·28 (7)		3056	3·27 (4)	

TABLE XIII.

Ortho Xylene.			Meta Xylene.			Para Xylene.		
$\Delta\nu$	λ_{Ra}	$\lambda_{i.r}$	$\Delta\nu$	λ_{Ra}	$\lambda_{i.r}$	$\Delta\nu$	λ_{Ra}	$\lambda_{i.r}$
			214	46·7 (1)				
			270	37·0 (0)		315	31·7 (1)	
			464	21·6 (0)		393	25·4 (0)	
586	17·06 (0)		530	18·9 (1)		460	21·7 (2)	
616	16·23 (0)					542	18·4 (0)	
651	15·36 (0)					644	15·5 (2)	
						694	14·4 (0)	
728	13·74 (2)	13·6 (s)	730	13·7 (2)				13·1 (f)
					13·0 (s)	784	12·76 (0)	12·58 (s)
816	12·25 (0)					828	12·08 (5)	11·9 (f)
					11·42 (s)			
						966	10·35 (0)	10·2 (f)
1000	10·00 (1)	10·2 (f)	1000	10·00 (2)	10·2 (f)	1009	9·91 (0)	
		9·78 (m)						
1052	9·51 (0)	9·50 (m)			9·68 (m)			9·62 (s)
					9·17 (s)			9·05 (s)
		8·92 (m)	1167	8·57 (0)	8·7 (f)	1158	8·64 (0)	8·6 (f)
						1208	8·28 (5)	
1239	8·07 (0)		1256	7·96 (2)		1248	8·01 (3)	
			1285	7·78 (1)		1296	7·72 (1)	
		7·25 (f)	1375	7·27 (0)	7·25 (f)	1376	7·27 (2)	7·25 (f)
1455	6·87 (0)	6·8 (s)	1462	6·84 (0)	6·77 (s)	1459	6·85 (1)	6·9 (s)
								6·35 (s)
1604	6·23 (0)	6·2 (m)	1610	6·21 (1)	6·2 (s)	1618	6·18 (3)	6·1 (s)
		5·25 (f)			5·25 (f)			5·3 (m)
2869	3·49 (1)		2869	3·49 (2)		2869	3·49 (2)	
2922	3·42 (2)		2915	3·43 (2)	3·38 (s)	2923	3·42 (4)	
3059	3·27 (2)	3·25 (s)	3036	3·29 (2)	3·25 ?	3041	3·29 (3)	3·25 ?



(a) Hg. spectrum, (b) heptane, (c) octane,
(d) cyclohexane, (e) diethyl ether, (f) water.

IX. *Ethers*

The two ethers diethyl ether and methylphenyl ether were studied. In the spectrogram of diethyl ether the aliphatic band corresponding to shift λ2871-2977 is the most prominent and consists of three lines of about the same intensity. All the strong infra-red absorptions obtained by Coblentz have corresponding Raman lines.

In phenyl-methyl ether we get the band at about $\Delta\nu$2900 which is characteristic of the aliphatic hydrocarbons and also the band at $\Delta\nu$3053 characteristic of the aromatics. The former band is resolved into two lines as in the case of methyl alcohol in approximately the same positions. As may be expected the Raman line at $\Delta\nu$ 999 is very prominent as in benzene.

Ethers.

TABLE XIV.

Diethyl ether.			Phenyl methyl ether.		
$\Delta\nu$	λ_{Ra}	$\lambda_{i.r}$	$\Delta\nu$	λ_{Ra}	$\lambda_{i.r}$
441	22·7 (3)		441	22·7 (0)	
798	12·53 (0)		627	15·95 (1)	
845	11·83 (3)	11·99 (s)	784	12·76 (0)	
928	10·78 (2)	10·75 (m)			
1027	9·74 (1)	9·6 (f)	999	10·01 (3)	
1082	9·24 (0)	9·25 (m)			
1150	8·70 (1)	8·75 (s)	1168	8·56 (1)	
1197	8·35 (0)				
1263	7·92 (1)	7·8 (s)	1234	8·10 (0)	
1334	7·50 (1)	7·3 } (s)	1441	6·94 (1)	
1457	6·86 (2)	7·0 }	1584	6·31 (1)	
		5·15 (m)	2815	3·55 (0)	
2871	3·48 (6)	3·45 (s)	2941	3·40 (0)	
2936	3·41 (6)		3053	3·27 (3)	
2977	3·36 (6)				

X. Cyclohexane (hexahydrobenzene)

It was shown in the previous sections that certain Raman lines appear to be characteristic of the aliphatic compounds and certain others of aromatic compounds. It would therefore be of great interest to study the Raman spectra of compounds showing the characteristics of both the aliphatics and aromatics. Hydroaromatic compounds (naphthene series) belong to this class. Although these possess the same structure as the aromatic compounds they differ from them in many points and show more resemblance to the aliphatic series. Cyclohexane was taken in our study as a typical example of this class of compounds. In spite of its similarity in structure to benzene this compound shows considerable differences in chemical behaviour, approximating in properties to the aliphatics. We may therefore consider how this resemblance to both aliphatic and aromatic compounds shown by this liquid is revealed by its Raman spectrum.

The most prominent feature of the spectrum of this liquid is the band corresponding to a shift of 2853-2935 wave numbers. This band appears in the same position as the one shown by all the aliphatic hydrocarbons. Comparing this band with the one present in pentane or heptane it is found that its width is somewhat less (by about 30 wave numbers) than in the former. Its structure is also somewhat different. In the paraffins the two edges of the band are the most intense, the lines between them being fairly sharp and bright. In cyclohexane the band is resolved into four components, a close intense doublet at the red end and a slightly brighter component on the violet end with a continuous spectrum in between. The fourth is a very weak line at about the middle of the band.

The other prominent lines in the spectrogram correspond to shifts of 800, 992, 1028 and 1445 wave numbers. Of

these the 992 shift is characteristic of benzene and $\Delta\nu$1028 and 1445 of aliphatic groups. $\Delta\nu$800 which is very prominent and sharp appears to be characteristic of this liquid.

The absence of $\Delta\nu$3060 very prominent in benzene and its derivatives may be noted.

The infra-red values given in the table are from J. Lecomte.

TABLE XV

Cyclohexane.

$\Delta\nu$	λRaμ	λ i. r.	$\Delta\nu$	λRaμ	λi. r.	$\Delta\nu$	λRaμ	λi.r
383	26·1 (0)				7·56 (f)			4·30 (f)
420	23·8 (0)		1346	7·43 (2)				3·90 (f)
478	20·9 (0)		1445	6·92 (3)	6.97 (s)	2853	3·51 (4)	3·60 (s)
608	16·4 (0)				6·17 (f)	2890	3·46 (1)	
800	12·50 (4s)	11·9 (s) 11·0 (m)			6·03 (f)	2921	3·42 (3)	
992	10·08 (2s)				5·67 (f)	2935	3·41 (3)	
1028	9·73 (2)	9·6 (m)			5·45 (f)			3·26 (f)
1157	8·64 (1)				5·15 (f)			3·16 (f)
1268	7·89 (3)	8·2 (s)			4·65 (f)			

XI. Pyridine

The great similarity of pyridine and benzene in chemical behaviour, such as their stability, the formation of hexahydride and the existence of three mono-substitution derivatives, suggests that the two have similar structure. The various formulae suggested by Körner, Rideal, and Bamberger are all similar to those suggested for benzene. The arrangement of the different atoms of the pyridine molecule in space is not

yet definitely known. A comparison of the Raman effect in the two liquids appears, however, to throw some light on the problem. From the following table which gives the shifts in wave-numbers between the exciting line and the Raman lines it will be found that several of them have al most identical values.

Benzene	$\Delta\nu$	605		849		991		1176			1592	3061
	Int.	(1)		(0)		(10)		(2)			(1)	(10)
Pyridine	$\Delta\nu$	603	651	885	935	988	1027	1157	1217	1376	1576	3056
	Int.	(1)	(3)	(1)	(0)	(10)	(10)	(1)	(2)	(1)	(2)	(10)

The two prominent values $\Delta\nu$ 991 and $\Delta\nu$ 3061 for benzene can certainly be identified with the values 988 and 3056 of pyridine. The Raman lines corresponding to $\Delta\nu$603 and $\Delta\nu$ 1576 which are relatively feebler in intensity also appear in both.

The similarities are even more striking on making a comparative study of the polarisation of the Raman lines in the two liquids. This was done spectroscopically by using a large nicol and taking spectrograms under identical conditions. It is found that the degrec of polarisation of the corresponding modified lines in benzene and pyridine is nearly the same. For instance, the modified line corresponding to $\Delta\nu$ 990 is the most intense and also the most strongly polarised in the two liquids. The correspondence in the degree of the different modified lines which appear in the scattered spectra of both pyridine and benzene suggests that the nuclear vibrations to which these lines correspond are identical in both cases. This means that the replacement of a CH group by N does not influence to an appreciable degree either the frequencies or the directions of vibrations of the other atoms. Thus the study of the Raman Spectra points

clearly a very close resemblance between the pyridine and benzene molecules.

It is found that the pyridine molecule has in addition to those of benzene, a few new characteristic frequencies, of which the one corressponding to $\Delta\nu$ 1027 is the most conspicuous. This additional prominent line appears to be generated by the substitution of N in place of the CH. groups. It is nearly as intense as the $\Delta\nu$ 988 line and is polarised also to nearly the same extent. These suggest a common origin for these two prominent modified lines. It may also be mentioned that pyridine gives a faint continuous spectrum in addition to the Raman lines.

TABLE XVI

Pyridine.

$\Delta\nu$	λRaμ	λi.r	$\Delta\nu$	λRaμ	λi.r	$\Delta\nu$	λRaμ	λi.r
405	24·69 (1)		935	10·69 (0)	10·53 (f)			6·95 (s)
603	16·58 (1)		988	10·12 (10)	10·08 (s)	1486	6·73 (0)	6·75 (f)
651	15·36 (3)		1027	9·73 (10)	9·73 (s)	1576	6·34 (2)	6·25 (s)
		13·3 (s)			9·35 (f)			5·2 (m)
		11·9 (f)	1157	8·64 (1)	8·78 (m)	3056	3·27(10)	3·25 (s)
		11·7 (f)	1217	8·21 (2)	8·26 (m)			2·91 (f)
885	11·30 (1)	11·28 (f)			7·75 (f)			
		10·85 (f)	1376	7·29 (1)	7·30 (f)			

XII. Quinoline

This liquid shows strong fluorescence, giving a continuous spectrum ranging from λ4200 to λ5050. The following Table gives the Raman lines excited by λ 4358·3A.U.

TABLE XVII

Raman lines.		$\Delta\nu$	λRa μ	λ infra-red.
Wave-lengh in A.U.	Wave-number in vacuo per cm.			
4405·9	22690	248	40·3	
4460·3	22414	524	19·1	
4515·0	22142	796	12·6	
4635·2	21568	1370	7·3	7·3
4682·0	21358	1580	6·3	6·2
5024·6	19897	3041	3·3	3·25

Of the above Raman lines the one at $\Delta\nu$ 3041 which is prominent may be identified with the well-known shift obtained in all aromatic hydrocarbons.

$\Delta\nu$ 1370 is the most prominent in the spectrum. Owing to the similarity in structure of this compound with naphthalene it was thought that a comparison of the Raman Spectra of the two would be of interest. We have therefore taken the Raman Spectrum of naphthalene, both fused and in carbon tetrachloride solution. Here also the Raman line shifted by 1378 wave-numbers is the most prominent. Corresponding to $\Delta\nu$ 524 in quinoline we get a Raman line at $\Delta\nu$ 529 in naphthalene which is also prominent.

It may be noted here that $\Delta\nu$ 1580 of quinoline occurs in benzene and its derivatives, pyridine and naphthalene. It is absent in the open chain compounds and may therefore be considered to be a characteristic of ring structure.

XIII. *Inorganic acids.*

Under this group sulphuric, hydrochloric and nitric acids were investigated by us. Sulphuric acid fresh from Kahlbaum's bottle was first tried and it showed such strong continuous spectrum that all but the strongest Raman lines were masked by it. However, on distillation in high vacuum most of the continuous spectrum disappeared and several Raman lines could clearly be identified and measured on the spectrogram.

In the case of hydrochloric acid two specimens were studied, one of 20 per cent. concentration distilled in vacuum, and another of 36 per cent. acid used as received from Kahlbaum (acids stronger than 20 per cent. could not be distilled at ordinary temperature). In spite of long exposures they showed only the water bands corresponding to about 3 μ and no Raman lines at all due to hydrochloric acid. This result is significant as it is in striking contrast with the case of the other two acids which show several prominent Raman lines. It is, however, easily understandable in view of the fact that when ionised the negative ions in the case of sulphuric and nitric acids are polyatomic and can therefore have characteristic vibrational frequencies in the infra-red region, while the question of such vibrational frequencies cannot naturally arise in the case of the Cl ion which is monatomic.

There is one i teresting result concerning the water band appearing in the spectrograms of hydrochloric acid of different concentrations which must be mentioned here. As the strength of the acid increases the band tends to sharpen appreciably as the following measurements on the limits of the band at λ 4701 and λ 4180 would show.

TABLE XVIII.

	HCl 0% (water)			HCl 20%			HCl 36%		
	λ. A. U.	Wave No. in vacuo per cm.	Band width in wave numbers.	λ. A. U.	Wave No. in vacuo per cm.	Band width in wave numbers.	λ. A. U.	Wave No. in vacuo per cm.	Band width in wave numbers.
Red edge ...	4770	20959		4767	20972		4741	21087	
Maximum ...	4701	21266	610	4704	21253	541	4701	21266	394
Blue edge ...	4635	21569		4647	21513		4654	21481	
Red edge ...	4222	23690		4222	23679		4204	23780	
Maximum ...	4180	23917	540	4182	23905	539	4173	23957	383
Blue edge ...	4126	24230		4128	24218		4146	24113	

It is evident from the above figures that while the maximum of each band occurs at the same wave length, the bands as a whole contract as the concentration increases.

In the case of nitric acid a specimen of 65% strength which had been distilled in vacuum was used for the investigation. Here, in addition to several prominent Raman lines appearing in the spectrogram, the water band also appears, which is however resolved distinctly into three separate lines. We shall return to this question of the influence of strong electrolytes on the structure of the water band in a later section of this paper (see Water).

Carelli, Pringsheim and Rosen[9] who have studied the Raman spectra of nitrates in solution get only the most prominent line appearing in nitric acid, *viz.*, that corresponding to a shift of 1045 wave numbers. They identify this frequency as an optically inactive frequency of the nitrate ion, which naturally is not represented in infra-red absorption measurements.

TABLE XIX.

Nitric acid.

$\Delta\nu$	λRaμ	λi.r.	$\Delta\nu$	λRaμ	λi.r.*	$\Delta\nu$	λRaμ	λi.r.
462	21·6(o)		951	10·51(2)	10·55(s)	3188	3·14(o)	
638	15·67(1)		1015	9·57(5)		3420	2·92(9)	Water
690	14·49(1)		1130	8·85(o)		3549	2·82(2)	Bands
			1305	7·66(4)	7·85(s)			

Sulphuric acid.

$\Delta\nu$	λRaμ	λi.r.	$\Delta\nu$	λRaμ	λi.r.*	$\Delta\nu$	λRaμ	λi.r.*
564	17·73(3)		1044	9·58(1)	9·55(s)	2043	4·90(o)	
909	11·01(3)	11·35(s)	1149	8·70(o)	8·6 (s)	2178	4·59(1)	
		10·4(s)			7·2 (f)	2372	4·22(o)	
								3·6(f)

[9] *Loc. cit.*

* Values obtained by Pfund from reflection measurements (Astro-physical Jour. Vol. XXIV, p. 19, 1906).

XIV. *Carbonates.*

Sodium and potassium carbonates were also investigated in solution. They gave only two Raman lines, one at λ 4570·0 excited by λ 4358·3 of the mercury arc, and the other at λ4298·8 excited by λ 4046·6. These lines obviously correspond to a shift of 1064 wave numbers. Kornfeld[10] and others have calculated the vibrational frequencies of the CO_3 ion as a whole (which would therefore be "inactive"). This frequency can be compared with the inactive 1045 of the NO_3 ion to which the CO_3 is well-known from recent X-ray investigations to bear a very close resemblance.

XV. *Water.*

We finally come to the case of water. The Raman spectrum of water has been investigated by a large number of workers and is known to show very broad bands, some of them extending over as large a range as 500 wave numbers. Since this is one of the few substances for which the Raman spectra exhibit diffuse bands and since our knowledge of the origin of the bands is very imperfect, we thought it desirable to investigate this substance in detail. The water was carefully purified dust-free by repeated slow distillution in vacuum in a double bulb made of pyrex glass and the spectrum was photographed with a high dispersion instrument.

The most conspicuous band is the one shifted from the exciting line by about 3400 wave-numbers (corresponding to about 3 μ). On a close examination this band shows a distinct structure. It seems to consist of three bands gradually shading into one another, the central one being the brightest, and the other two being feebler in comparison. The one on the shorter wave-length side is a little less than twice as

[10] H. Kornfeld. Z. fur physik. Vol. 26, p, 205, 1924,

far removed from the central band as that on the red side ; the infra-red wave-length corresponding to the three bands being 2·77μ, 2·90μ, and 3·13μ respectively. In addition to these bands there are present two other faint bands corresponding to the infra-red wave lengths 1·82μ and 4·25μ. The following table gives the measurements of the Raman spectrum in water.

TABLE XX

Exciting lines.		Modified lines.			Frequency difference.
λ	Wave No. in vacuo.	λ	Wave No. in vacuo.	Intensity.	
3650·1	27389				
		4139·6	24150	Medium	3239
		4183·2	23898	Strong.	3491
		4567·6	21887	Faint.	5502
4046·6	24705				
		4473·0	22350	Faint.	2355(?)
		4640·0	21546	Medium.	3159
		4700·6	21268	Strong.	3437
		4739·0	21096	Medium.	3609
4358·3	22938	5125·0	19507	Medium.	3431
				Mean shift	2355 3199 3458 3609 5502
				$\lambda_{Ra}\mu$.	4.25(?) 3·13 2·90 2·77 1·82

The Raman spectrum of crystal ice photographed with the same spectrograph revealed three bands *more or less sharp* and distinctly resolved from one another whose shifts from the exciting line correspond to 2·82μ, 2·95μ and 3·13μ respectively. These values for the water bands in ice are in

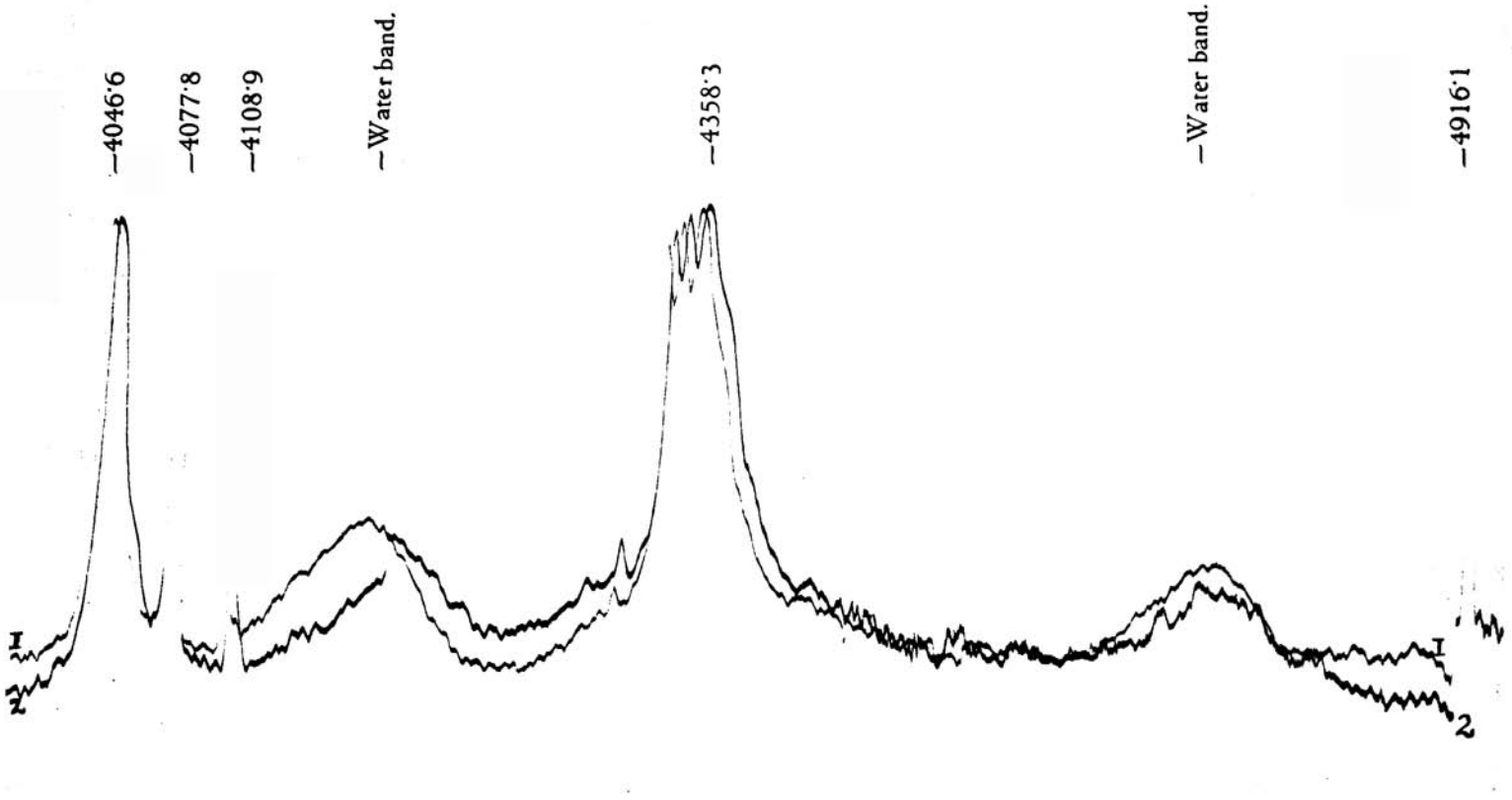
excellent agreement with the values obtained by Krishnan for the Raman bands due to the water of crystallisation in selenite crystal ($CaSO_4$ $2H_2O$), *viz.* 2·86μ, 2·94μ and 3·09μ.

These bands can immediately be identified with the three bands obtained with water in practically the same positions ; only in the latter case they are so diffuse and they encroach so much on one another that they can be only just recognised as three.

This widening of the water bands as we pass from the crystalline state to that of a liquid is very significant and is probably connected with the freedom of rotation of the molecules which exists in the liquid state and which is not present—at least not to the same extent—in the crystalline state. The continual collision between the molecules will considerably hamper their free rotation, and the rotational frequencies will therefore not be well defined and would extend over an appreciable range. If we now postulate that these rotational frequencies can combine with the characteristic frequencies of the molecules, the breadth of the Raman bands for water, as contrasted with their sharpness in ice, is readily understood. In connection with this explanation of the widening of the bands as we pass from the crystal to the liquid, attention may be drawn to a very general observation that amorphous solids give rise to diffuse Raman bands as contrasted with the relatively sharp lines appearing in the spectrum of the light scattered by crystals. Even in the case of crystals like quartz which give very sharp Raman lines at the room temperature, it has been found by Krishnan[11] that the lines get very diffuse when the temperature is raised to about 130°C. Brickwedde and Peters[12] working

[11] K. S. Krishnan, Nature, Vol. 122, p. 477, 1928.

[12] F. G. Brickwedde and F. Peters, Bulletin, Amer. Phy. Soc., Vol. III, Nov. 15, 1928.



Microphotometered Raman spectra of (1) Water at 30°C, and (2) Water at 80°C.

with quartz over a much larger range of temperatures have also observed a similar broadening at higher temperatures.

The 3μ Raman band of water has also been investigated by us at different temperatures. Two spectrograms under identical conditions of illumination, exposure, etc. are taken side by side in the same plate, one at 30°C and the other at 80°C. The 3μ band shows an interesting result. Of the three imperfectly resolved components of this band, the one corresponding to the shortest shift, *i.e.*, 3·13μ component, practically disappears at a temperature of 80°C, while the other two components, *viz.* 2·90μ and 2·77μ show only a very slight diminution in intensity—which, of course, we should expect owing to the small decrease in the density of water at the higher temperature. These results are clearly brought out on comparing the micro-photometer records of the two spectrograms. (See Plate IX).

The disappearance of the 3·13μ component at high temperatures is a surprising result which is not easily understood. It is well-known that water behaves anomalously in regard to most of its molecular properties; and it has been suggested from various independent considerations that it shows a very conspicuous tendency to polymerisation even at room temperature, the polymers rapidly breaking up as the temperature is raised. Whether the disappearance of the 3·13μ component of the Raman water band has anything to do with the breaking up of the complex molecules of the type $(H_2O)_n$ which exist in appreciable proportions at ordinary temperatures, is more than we can venture to answer with the data at our disposal.*

* In fact the influence of the polymerisation of water on the characterstic frequencies of the medium figures very prominently in discussions by Coblentz, Lecomte, Collins and others on the infra-red absorption bands of water, and it is therefore only natural to try whether the present experimental result is also not explicable on the same basis.

It may not be out of place, in this connection, to draw attention to a remarkable result concerning the nature of the Raman water bands in aqueous solutions of electrolytes. There is a general tendency for the three components of the water band, as already mentioned in an earlier section, to get *sharper* as the concentration of the electrolyte is increased. In fact with 65% nitric acid the bands are almost *as sharp as in crystalline ice.* The result is very significant in view of our present ideas regarding the constitution of electrolytic solutions, according to which their "fine structure" tends to simulate in a sense that of a crystal.

Ice

The modified scattering in ice was first studied by Prof. Raman.[13] Even in the very first paper in which he announced the new effect he records observations where the light from a mercury arc was scattered by a large block of clear ice and the diffused radiations spectroscopically analysed. It was found that "the solid crystal ice showed the sharp modified lines in the scattered spectrum in approximately the same positions as pure water." A more detailed study of the effect in ice was made by Rao [14] who found that compared with the case of water, the bands observed with ice were sharper and of shorter wave-length. He gives the values $2 \cdot 99\mu$ for water and $3 \cdot 10\mu$ for ice. The experiment was repeated by Krishnan with an E_2 quartz spectrograph. He found the 3μ band resolved into two narrow bands. Mr. Bakshi working in this laboratory took a series of photographs in large blocks of clear crystalline ice. The measurements recorded here were made on one of his plates.

[13] C. V. Raman, *loc. cit.*

[14] I. Ramakrishna Rao, Ind. Journ. Phy. Vol. III, p. 131, 1928.

TABLE XXI

Exciting Lines.		Raman Lines.			Frequency Difference.			
λ.	Wave No. in Vacuo.	λ.	Wave No. in Vacuo.	Intensity.				
3650·1	27389	...	...	...	...	...	...	...
...	...	4131·6	24197	Medium	3192	...	...	...
...	...	4165·3	24001	Medium	...	3388	...	...
...	...	4545·0	21996	Faint	..	...	...	5393
4046·6	24705	...	...	...	...	...	...	...
...	..	4647·8	21510	Medium	3195	...	...	...
...	...	4691·2	21311	Medium	...	3394	...	...
...	...	4725·5	21156	Faint	...	...	3549	...
...	...	...	...	...	...	...	...	...
				mean $\Delta\nu$	3193	3391	3549	5393
				$\lambda_{Ra}\mu$.	3·13	2·95	2·82	1·85

All the four bands are much narrower than in the case of water and appear to be slightly shifted towards the shorter wave-length side. In the case of water the $2 \cdot 90\mu$ band is much brighter than the $3 \cdot 13\mu$ band, while in ice the intensity of both these bands is about the same. The $1 \cdot 85\mu$ band is relatively much brighter in ice than in water.

In view of the remarks that were made in the section on water, it will be interesting to compare the structure of the water bands as they appear in different substances. The following table shows the collected data, the numbers representing the corresponding infra-red absorption wave-length in μ.

TABLE XXII

Water ...	4·25(?)	3·13	2·90	2·77	1·82
Ice ...	...	3·13	2·95	2·82	1·85
Selenite ...	...	3·09	2·94	2·86	...
Nitric acid ...	...	3·14	2·92	2·82	...

General Discussion of Results.

As has been repeatedy emphasised by Prof. Raman, the difference in frequency between the incident radiation and any one of the Raman lines excited by it should be equal to a characteristic frequency of the medium. The question naturally arises how these frequencies calculated from the Raman spectrum compare with the values obtained by other independent methods, *e.g.*, from the maximum of absorption in the infra-red, or from the maximum of reflection from the surface of the medium. The latter method has not been widely used for the investigation of molecular frequencies. But we have very reliable measurements on the absorption spectra in the infra-red for almost all the substances investigated by us from the classic researches of Coblentz and others.* These values have been exhibited side by side, with the characteristic frequencies calculated from the Raman spectra, in the series of Tables given in the last section.

The relative intensities and the presence or absence of the corresponding Raman and infra-red absorption lines for a few typical liquids are brought out clearly in the Table given below.

TABLE XXIII

Raman lines.	Infra-red absorption lines.	Pyridine.	Octane.	Nitro-methane.	Chloroform.	Carbon disulphide.
...	...	μ	μ	μ	μ	μ
Strong	Strong	3·27,6·34,9·7, 10·1,	3·4,6·86, 8·78.	3·38.7·16, 10·92	3·31,6·9,8·2	...
Weak	Weak	11·3,10·69, 6·73,7·2, 8·26	7·89,9·27, 10·36,12·3	...	...	...
Strong	Weak	...	8·66, 11·16 to 11·61	...	...	...
Weak	Strong	8·64	7·37	6·41,9·0	...	...
Absent	Strong	5·2,6·95	13·8,5·82	13·96	4·4,9·6, 10·82.11·8	4·6,6·8,11·6, 13·4
Strong	Absent	...	7·17,7·69, 9·68	...	...	12·5,15·27

*For a good collection of data on the infra-red absorption spectra, see J. Lecomte "Le Spectre Infrarouge."

On a critical inter-comparison of these two sets of values for the characteristic frequencies of the medium the following facts emerge :—Although there is a *general* correspondence between them there are also very striking differences; for example a large number of frequencies appear in the Raman spectra which are not represented in infra-red absorption, and similarly also there are many strong absorption frequencies which do not produce the Raman lines. Even among the frequencies which appear simultaneously in absorption and in Raman spectra their relative intensities are often times widely discrepant in the two. Further, the agreement even in these cases between the Raman molecular frequencies and the corresponding absorption frequencies is far from being satisfactory.

The last statement is not difficult to understand. The theoretical investigations of Foesterling [15] and others have shown that the maximum of reflection or of absorption need not always coincide with the actual frequency of the medium, but may be slightly shifted with respect to it, the shift of course being capable of evaluation in simple cases. From this point of view the Raman spectrum gives us uniquely the natural frequencies of the medium in a manner, the infra red measurements either of absorption or of selective reflection are not capable of giving.

However, neglecting for the present the *small* differenees between absorption maxima and the natural frequencies which give rise to them, it is hardly necessary to remark that every absorption maximum must necessarily point to the existence in that region of the spectrum a characteristic frequency. In the same manner every Raman line must also correspond to a natural frequency. The question therefore naturally arises why corresponding to every Raman line

[15] Foesterling :—Ann. der. Phys. Vol. 61, p. 577. 1920. See also Landsberg and Mandelstam, Compt. Rend. Vol. 187 p. 109, 1928.

we should not have an absorption maximum in the infra-red and *vice-versa.* In order to be able to answer this question satisfactorily it would be necessary to understand under what conditions a given infra-red frequency of the medium appears in absorption spectrum, and under what other conditions it produces the corresponding Raman line.

As has been pointed out recently by Langer[16] and Dieke[17], the wave mechanical treatment of the problem of dispersion throws considerable light on this point. If initially the atom or molecule is in one of its discrete levels of energy given by say E_k, and a transition of the molecule from this level to another level of energy, say equal to E_l, is possible (*i.e.* is not forbidden by the usual rules of selection), then the molecule is capable of absorbing the particular frequency given by $\nu_{kl} = \frac{E_l - E_k}{h}$. On the other hand, if the same frequency ν_{kl} is to appear as a Raman line in the spectrogram of the light scattered by the molecule, according to Schrödinger we have to start not with a singleeigen state but with an initial *simultaneous existence* of the molecule in the two states represented by k and l and further, transitions ought to be possible for the molecule from either of the states k and l to at least a third discrete level of energy represented by say n. It must be pointed out here that *it is immaterial whether the transitions* $k \rightarrow l$ *are themselves forbidden or not.*

Thus it is obvious that the condition that has to be satisfied before a frequency ν_{kl} can appear as an absorption line, is entirely different from that which has to be satisfied if the same frequency is to combine with an incident frequency to give a Raman line. If the transition ν_{kl} is forbidden there would not be any absorption corresponding to this frequency;

[16] R. M. Langer. Nature, Vol. 123, p. 345, March 9, 1929.
[17] G. H Dieke. Nature, Vol. 123 p. 564, April 13th, 1929.

whereas if a third level n can be found to which transitions separately from k and from l are possible the same ν_{kl} would give rise to a Raman line. On the other hand, the transition $k \rightarrow l$ may be possible, but still there may not be a third level n satisfying the above requirements, in which case we would get it only as an absorption line, and not as a Raman line.

However, before we can apply these rules to any specific case we must know beforehand the quantum designations of the different energy levels in which the molecules are capable of existing in order to be able to say uniquely which of the transitions between the different levels are permissible. Until we are in a position to do this we cannot say *apriori* which of the frequencies would give rise to a Raman line, and which of them would appear as an absorption line and which others again would appear simultaneously as a Raman line and as an absorption line. In the case of simple molecules like hydrogen or nitrogen or carbondioxide where it is possible to calculate the different energy levels, the above ideas have been verified by Rasetti [18]. But the compounds investigated by us, are, however, far too complicated to be amenable to calculation ; and beyond understanding in a very general way the mere fact of want of correspondence between the infra-red and Raman molecular frequencies, we are not in a position to explain (and much less to predict) the exact nature of the correspondence.

There is, however, one interesting conclusion in connection with the " third " level necessary for the excitation of the Raman spectra which may be mentioned with some certainty. It can easily be shown that the intensity of the Raman lines corresponding to the change of frequency ν_{kl} must be particularly intense as the frequency of the *exciting* line approaches the value $\frac{E_n - E_k}{h}$ where E_n is the energy

[18] F. Rasetti. Nature, Vol. 123, p. 757, May 18, 1929.

of the "third" level mentioned in the previous section. It is an experimental fact that the intensity of the Raman lines increases very rapidly with the frequency of the exciting line, in fact even more rapidly than Rayleigh's λ^{-4} law.[19] When we combine this fact with the theoretical relation stated above regarding the intensity of excitation, we are led to the conclusion that as we proceed towards the ultraviolet we are continually approaching the frequency $\frac{E_n - E_k}{h}$; since $\frac{E_k}{h}$ is an infra-red frequency, E_n must correspond to a region in the ultraviolet sufficiently removed from the visible part of the spectrum. Of course this statement regarding E_n is not precise, since the observed intensity is an integrated effect which includes all the different "third" levels denoted by E_n; and we may therefore modify it by saying that the "third" levels involved in the Raman scattering are *predominantly* in the ultra violet. The relative influences of the different "third" levels find a parallel in the influences of natural frequencies in classical dispersion.

The Polarisation of the Raman lines.

The polarisation of the Raman lines for some typical liquids was also investigated. The strong Raman radiation corresponding to a shift of 3000 wave numbers which as we have mentioned is characteristic of the hydrocarbons is of special interest. While this radiation is very strongly polarised in the aliphatics, it shows a considerable imperfection of polarisation in the aromatics. This statement is true in a general way of the other Raman lines also, and in this respect the polarisation of the Raman lines bears a very close analogy to that of the classical scattering in these two types of

[19] See C. V. Raman and K. S. Krishnan. Proc. Roy. Soc. Vol. 122, p. 23, Jan. I, 1929

compounds. The analogy acquires a special significance in view of what has been said in the previous section regarding the electronic nature of the frequencies of the "third" levels; because this fact points to a very much closer relation between the two types of scattering than is apparent at first sight.

In conclusion, we wish to thank Sir C. V. Raman, F.R.S. for his inspiring guidance and Mr. K. S. Krishnan for his valuable suggestions and kind interest in the work.

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Paraffins.

TABLE XXIV.

n. Pentane $CH_3(CH_2)_3.CH_3$

Raman lines.		Exciting line. λ A.U.	Δ ν	Raman lines.		Exciting line λ. A.U.	Δ ν
Wave No. in Vacuo per cm.	Intensity.			Wave No. in Vacuo per cm.	Intensity.		
24452	2d	3650·1	2937	22463	0	4358·3	475
24420	4d	,,	2969	22172	1	,,	766
24390	2d	3654·8	2964	22099	1	,,	839
24363	0	4046·6	342	22060	0	,,	878
24227	1d	4046·6	478	22034	0	,,	904
23939	1d	,,	766	21974	1	,,	964
23866	1d	,,	839	21899	1	,,	1039
23845	0d	,,	860	21851	2	4046·6	2854
23799	0d	,,	906	21828	4d	,,	2877
23680	1d	,,	1025	21795	2 ,,	,,	2910
23633	1	,,	1072	21767	3 ,,	,,	2938
23542	1	,,	1163	21742	3 ,,	,,	2963
23403	1	,,	1302	21633	2	4358·3	1305
						4077·8	2883
23344	0	,,	1361	21585	0	4358·3	1355
						4077·8	2931
23302	0	,,	1403	21555	1	4358·3	1383
						4077·8	2961
23247	3 broad	,,	1458	21474	4 v.b.	4358·3	1464
22795	2	4358·3	143	20063	3 d	,,	2875
22659	0d	,,	279	20037	2	,,	2901
22592	0d	,,	346	20002	2	,,	2936
22537	2s	,,	401	19977	2	,,	2961

TABLE XXV

n. Heptane. $CH_3.(CH_2)_5.CH_3$

Raman lines.		Exciting lines λ. A. U.	Δν	Raman lines.		Exciting lines λ. A. U.	Δν
Wave No. in vacuo per cm.	Intensity.			Wave No. in Vacuo per cm.	Intensity.		
24471	1	3650·1	2918	22629	1	4358·3	309
24452	1	,,	2937	22531	1	,,	407
24424	3	,,	2965	22492	2	,,	446
24389	1	3654·8 4046·6	2965 316	22439	0	,,	499
24363	1	4046·6	342	22392	1	,,	546
24257	0	,,	448	22218	0	,,	720
24206	0	,,	499	22169	3 s	,,	769
24159	0	,,	546	22095	2	,,	843
23936	3	,,	769	22034	2	,,	904
23879	0	,,	826	21971	2 d	,,	967
23859	0	,,	846	21903	2	,,	1035
23804	0	,,	901	21854	4	4046·6	2851
23737	0 d	,,	968	21833	2	,,	2872
23672	2	,,	1033	21798	2	,,	2907
23617	1	,,	1088	21771	4	,,	2934
23572	0	,,	1133	21742	3	,,	2963
23543	1	,,	1162	21690	1	4358·3	1248
23494	0	4077·8	1022	21668	1	,,	1270
23464	0	4046·6	1241	21634	2	4358·3 4077·8	1304 2882
23442	0	,,	1263	21588	2	4358·3 4077·8	1350 2928
23401	1	,,	1304	21549	1	4358·3 4077·8	1389 2967
23359	0 b.	,,	1346	21488	2 d	4358·3	1450
23305	0 b.	,,	1400	20084	4	,,	2854
23249	4 b.	,,	1456	20066	3	,,	2872
22791	1 s	4358·3	147	20016	4	,,	2922
22664	0	,,	274	19980	4	,,	2958

TABLE XXVI

n. Octane. $CH_3.(CH_2)_6.CH_3$.

Raman lines.		Exciting lines. λ. A.U.	$\Delta\nu$	Raman lines.		Exciting lines. λ. A.U.	$\Delta\nu$
Wave No. in Vacuo per cm.	Intensity.			Wave No. in Vacuo per cm.	Intensity.		
27006	1	3341·5	2912	23349	0	4046·6	1356
26252	1*d*	3650·1	1137	23312	0	,,	1393
26217	1*d*	3654·8	1137	23258	2*vb*	,,	1447
26129	0	3650·1	1260	22782	0*b*	4358·3	156
26089	2*d*	,,	1300	22657	0*d*	,,	282
26050	1*d*	,,	1339	22124	0*d*	,,	814
26017	1*d*	3654·8	1337	22080	0	,,	858
25987	1*d*	3650·1	1402	22041	0*d*	,,	897
25948	2*b*	,,	1441	21969	1*d*	,,	969
25891	2	3654·8	1463	21907	0	,,	1031
25842	1*b*	3663·3	1448	21855	4	4046·6	2850
24534	1*d*	3650·1	2854	21832	2*d*	,,	2873
24455	0	,,	2934	21798	2*d*	4046·6	2907
24420	3*d*	,,	2969			4358·3	1140
24392	2*b*	3654·8	2962	21767	3*d*	4046·6	2938
24369	0	4046·6	336	21742	2*d*	,,	2963
24353	2	,,	352	21662	0*d*	4358·3	1276
23841	0	,,	864	21639	1*d*	4358·3	1299
						4077·8	2877
23810	1	,,	895	21581	0*d*	4358·3	1357
						4077·8	2925
23741	1*b*	,,	964	21551	0*d*	4358·3	1387
						4077·8	2965
23671	0	,,	1034	21486	2*v.b.*	4358·3	1452
23626	0*v.b.*	,,	1079	20089	1*d*	,,	2849
23565	0	,,	1140	20001	1*d*	,,	2937
23550	0	,,	1155	19976	1*d*	,,	2962
23387	2*d*	,,	1318				

TABLE XXVII

Chloroform $CHCl_3$.

Raman lines.		Exciting line λ. A.U.	Δν	Raman lines.		Exciting line λ. A.U.	Δν
Wave Nos. in Vacuo per cm.	Intensity.			Wave Nos. in vacuo per cm.	Intensity.		
25371	0	4046·6	−666	23199	4	4358·3	−261
25070	3	4046·6	−365	22731	0	4347·5	264
24965	3	4046·6	−260	22676	6	4358·3	262
24445	4*d*	4046·6	260	22633	0	4347·6	362
24370	3*d*	3650·1	3019	22568	7	4358·3	370
24273	1	3663·3	3017	22324	1	4347·5	671
24255	2	4077·8	261	22270	8	4358·3	668
24148	3*d*	4077·8	368	22172	3*d*	4358·3	766
24087	6	4046·6	668	21721	1*d*	4358·3	1217
23944	3*d*	4046·6	761	21684	4*d*	4046·6	3021
23847	2*d*	4077·8	669	21497	2	4358·3	1441
23758	0	4077·8	758	19921	2*d*	4358·3	3017
23603	1*d*	4358·3	−665	18572	1*d*	5460·7	−264 incident.
23486	2*d*	4046·6	1219	18049	3*d*	5460·7	259 incident.
23303	8	4358·3	−365	17945	2	5460·7	363
23254	0	4046·6	1451				

Table XXVIII.

Bromoform $CHBr_3$.

Raman lines.		Exciting line λ. A.U.	Δν	Raman lines.		Exciting iine λ. A.U.	Δν
Wave Nos. in vacuo per cm.	Intensity.			Wave Nos. in vacuo per cm.	Intensity		
27613	0	3650·1	−224	24486	2	4046·6	219
				24370	0	3650·1	3019
27509	0	3663·3	−155	24168	2	4046·6	537
27239	0	3650·1	150	24048	1*d*	4046·6	657
27198	0	3654·8	156	23159	2	4358·3	−221
27132	0	3663·3 3654·8	158 222	23094	2	4358·3	−156
27065	0	3663·3	225	22784	3	4358·3	154
26847	0	3650·1	542	22714	3	4358·3	224
26732	0	3650·1	657	22398	2	4358·3	540
24930	1	4046·6	−225	22280	2*d*	4358·3	658
24859	1	,,	−154	21684	0	4046·6	3021
24553	2	,,	152				

TABLE XXIX
Carbon tetrachloride. CCl_4

Raman lines.		Exciting line λ A.U.	Δ ν	Raman lines.		Exciting line λ A.U.	Δ ν
Wave Nos. in vacuo per cm.	Intensity.			Wave Nos. in vacuo per cm.	Intensity.		
27139	0	3654·8	215	23943	2d	4046·6	762
27076	2	3650·1	313	23914	2d	4046·6	791
27042	0	3654·8	312	23393	1	4358·3	—455
26929	3	3650·1	460	23248	2	4358·3	—310
26896	0	3654·8	458	23154	3	4358·3	—216
26830	0	3663·3	460	22778	0	4347·5	217
26625	1	3650·1	764	22718	5	4358·3	220
26597	1	3650·1	792	22679	0	4347·5	316
25162	0	4046·6	—457	22623	7	4358·3	315
25017	1	4046·6	—312				
24920	2	4046·6	—215	22535	0	4347·5	460
24492	4	4046·6	213	22480	8	4358·3	458
24391	4	4046·6	314	22177	2	4358·3	761
24299	0	4077·8	217	22149	2	4358·3	789
24247	5	4046·6	458	21403	0	4358·3	1535
24207	0	4077·8	309				
24056	0	4077·8	460				

TABLE XXX
Carbon disulphide CS_2

Raman lines.		Exciting line λ A.U.	Δ ν	Raman lines.		Exciting line λ A.U.	Δ ν
Wave Nos. in vacuo per cm.	Intensity.			Wave Nos. in vacuo per cm.	Intensity.		
24048	5*s*	4046·6	657	22284	10*s*	4358·3	654
23903	1*d*	4046·6	802	22142	3*dr*	4358·3	796
23860	2*s*	4077·8	650	19676	0*d*	4916·1	660
23593	4*s*	4358·3	—655	17650	8*s*	5460·7	658
22385	1	4339·2	654	17505	1*d*	5460·7	803
22342	2	4347·5	653				

Alcohols.

Table XXXI

1. Methyl alcohol. $CH_3 \cdot OH$

Raman lines.		Exciting lines λ A. U.	Δ ν	Raman lines.		Exciting lines λ A.U.	Δ ν
Wave Nos. in vacuo per cm.	Intensity.			Wave Nos. in Vacuo per cm.	Intensity.		
				23245	1*b*	4046·6	1460
26358	1	3650·1	1031	21908	1	4358·3	1032
25924	1*vd.*	,,	1465	21875	3	4046·6	2830
24555	1	,,	2834	21767	3	,,	2938
24450	1 b.	,,	2939	21681	0	4358·3	1257
24404	1	3654·8	2950	21578	1*d*	,,	1360
	Band	3650·1		21476	1*d*	,,	1462
23674	1	4046·6	1031	20107	1	,,	2831

Table XXXII

2. Ethyl alcohol. $CH_3 \cdot CH_2 \cdot OH$

Raman lines.		Exciting lines.	Δ ν	Raman lines.		Exciting lines.	Δ ν
Wave Nos. in vacuo per cm.	Intensity.			Wave Nos. in vacuo per cm.	Intensity.		
24460	1	3650·1	2929	21891	0	4358·3	1047
24419	2	,,	2970	21829	2*b*	4046·6	2876
23823	3	4046·6	882	21773	4	,,	2932
		Band		21728	3*b*	,,	2977
23658	1*b*	4046·6	1047	21669	0	4358·3	1269
23430	1	,,	1275	21584	0	4046·6	3121
23235	2	,,	1470	21485	1	4358·3	1453
22488	0	4358·3	450	20070	0	,,	2868
22052	2*s*	,,	886	20010	0	,,	2928

TABLE XXXIII

3. Propyl alcohol. $CH_3.CH_2.CH_2.OH$.

Raman lines.		Exciting lines λ. A.U.	Δ ν	Raman lines,		Exciting lines λ. A.U.	Δ ν
Wave Nos. in vacuo per cm.	Intensity.			Wave No. in vacuo per cm.	Intensity.		
26104	0	3650·1	1294	21968	1	4358·3	970
26025	0	,,	1364	21879	0	,,	1059
25931	0	,,	1467	21823	4	4046·6	2882
24460	0	,,	2929	21791	3*d*	,,	2914
24407	1	,,	2972	21757	3*d*	,,	2948
24381	0	3654·8	2973	21739	2*d*	,,	2966
24248	0	4046·6	457	21645	0	4358·3	1293
23847	2	,,	858	21574	0	4077·8	2942
23735	0	,,	970	21475	2	4358·3	1463
23638	0	,,	1067	20074	1	4358·3	2864
23424	0	,,	1281	20026	1	,,	2912
23243	1	,,	1462	19996	1	,,	2942
22488	1	4358·3	450				
22068	2	,,	870				

TABLE XXXIV

Isopropyl alcohol $(CH_3)_2$. CH.OH

Raman lines.		Exciting lines λ.A.U.	Δν	Raman lines.		Exciting lines λ.A.U.	Δν
Wave No. in vacuo per cm.	Intensity.			Wave No. in vacuo per cm.	Intensity.		
24466	2d	3650·1	2923	22117	6s	4358·3	821
24447	,,	,,	2942	21983	4dv	,,	955
24413	4d	,,	2976	21895	0	,,	1043
24376	2d	3654·8	2978	21826	4d	4046·6	2[illegible]
24270	0	4046·6	435	21787	2d	,,	2[illegible]71
24216	0	,,	489	21767	2d	4046·6	2938
23886	6s	,,	819			4358·3	1141
23750	2dv	,,	955	21729	6d	4046·6	2976
23697	1s	,,	1008	21632	1d	4077·8	2884
23641	0d	,,	1064	21599	0	4358·3	1339
23560	1d (double)	,,	1145	21580	2d (double)	4077·8	2936
23363	1d	,,	1342	21538	2d	,,	2978
23252	2dr	,,	1453	21483	3dr	4358·3	1455
22783	0d	4358·3	155	20278	0	,,	2665
22628	0d	,,	310	20213	0	,,	2725
22566	0d	,,	372	20059	4d	,,	2879
22506	2d	,,	432	20019	3d (Not well resolved.)	,,	2919
22450	1d	,,	488	20001	3d (Not well resolved.)	,,	2937
22202	0	,,	736	19964	5d	,,	2974
22177	0	,,	761				

TABLE XXXV

Isobutyl alcohol $(CH_3)_2$. CH. CH_2OH.

Raman lines.		Exciting lines λ. A. U.	Δν	Raman lines.		Exciting lines λ.A. U.	Δν
Wave No. in vacuo per cm.	Intensity.			Wave No. in vacuo per cm.	Intensity.		
24.41	3d (double)	3650·1	2949	21887	0	4358·3	1051
210	2d	4046·6	495	21830	5 dr	4046·6	2875
2[illegible]888	4	,,	817	21741	5dr (Very broad not resolved properly)		2964
28742	1d	,,	964	21643	3d (Very broad not resolved properly)	4077·8	2873
23659	0	,,	1047				
23576	1d	,,	1129	21596	1d	4358·3	1342
23454	,,	,,	1251				
23363	,,	,,	1342	21548	2d	4077·8	2968
23241	,,	,,	1464	21477	4d	4358·3	1461
22788	,,	4358·3	150?	20278	0	,,	2665
22544	1 v. b.	,,	394	20213	0	,,	2725
22443	2d	,,	495	20065	4dr	,,	2873
22149	1	4347·5 / 4358·3	846 / 789	19971	5dr	,,	2967
22117	5	4358·3	821				
22029	0	,,	910				
21977	3 d v.	4046·6 / 4358·3	2728 / 961				

TABLE XXXVI

β Isoamyl alcohol $(CH_3)_2$. $CH.CH_2.CH_2OH$.

Raman lines		Exciting lines λ.A.U.	Δν	Raman lines.		Exciting lines λ.A.U.	Δν
Wave No. in vacuo per cm.	Intensity.			Wave No. in vacuo per cm.	Intensity.		
26626	1	3650·1	763	23645	1 v.d	4046·6	1060
26596	0	3654·8	758	23571	,,	,,	1134
26563	2	3650·1	826	23534	0	,,	1171
26450	0d	,,	939	23374	0 b.	,,	1331
26339	0	,,	1050	23248	4	,,	1457
26266	0b	,,	1123	22718	0	4358·3	220
26223	0b	,,	1166	22597	0	,,	341
26103	0	,,	1286	22493	0	,,	445
26063	0	,,	1326	22418	0	,,	520
25939	3v.b	,,	1450	22169	2	,,	769
25842	1d	3663·3	1448	22104	2	,,	834
25733	0	3650·1	1656	21980	1	,,	958
24423	3	,,	2966	21924	1	,,	1014
24385	0	3654·8	2969	21829	8	4358·3	1109
24249	0d	4046·6	456			4046·6	2876
23937	2	,,	768	21723	8	4046·6	2982
23875	3	,,	830	21592	2	4358·3	1346
23811	0b	,,	894	21472	4	,,	1466
23753	1v.d	,,	952	20058	4	,,	2880
23697	,,	,,	1008	19980	3		2958

TABLE XXXVII.

Allyl alcohol $CH_2 : CH.CH_2OH$.

Raman lines.		Exciting lines λ. A. U.	Δν	Raman lines.		Exciting lines λ. A. U.	Δν
Wave No. in Vacuo per cm.	Intensity.			Wave No. in Vacuo per cm.	Intensity.		
26843	0	3650·1	548	23473	1	4077·8	1043
26737	0	,,	652	23414	4	4046·6	1291
26473	1	,,	916	23369	0	,,	1336
26436	1	3654·8	918	23289	2 d	,,	1416
26262	1	3650·1	Two lines not realvd.	23238	3	,,	1467
26104	3	3650·1	1285	22647	0	4358·3	291
26066	2	3650·1	1323	22577	0	,,	361
		3654·8	1288	22495	2 v.d.	,,	443
26004	1	3663·3	1286	22444	0	,,	494
25966	1	3650·1	1423	22387	0	,,	551
25920	1	,,	1469	22295	0 d	,,	643
25838	0	3663·3	1452	22024	1 v. d.	,,	914
25745	5	3650·1	1644	21940	0	,,	998
25709	2	3654·8	1645	21907	0	,,	1031
24376	2	3650·1	3013	21837	2 b	,,	1101
						4046·7	2868
24274	4 v. d.	4046·6	431	21777	2 b	4358·3	1161
						4046·7	2928
24206	1 v. d.	,,	499	21693	4	4046·6	3012
24151	1	,	554	21649	2	4358·3	1289
24073	0.b.	,,	632	21610	2	,,	1328
23951	0. v.b.dr	,,	754	21503	1 b.	,,	1435
23803	2	,,	902	21339	0	4347·5	1656
23709	2	,,	996	21284	3	4358·3	1654
23674	2	,.	1031	19921	0	,,	3018
23597	0. v.d.	,,	1108	19859	1	,.	3079 P
23556	0	,,	1149	...	...	...	...

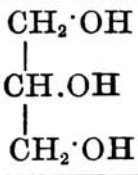
TABLE XXXVIII.

Phenol C_6H_5OH.

Raman lines.		Exciting lines λ A. U.	Δν	Raman lines		Exciting lines λ. A. U.	Δν
Wave no. in Vacuo per cm.	Intensity.			Wave no. in Vacuo per cm.	Intensity.		
26857	1	3341·5	3061	22114	1	4358·3	824
26771	1	3650·1	618	21991	0	4347·5	1004
26626	0	,,	763	21930	2	4358·3	1008
26577	2	,,	812	21760	0	,,	1178
26026	0.d.	,,	1363	21642	2	4046·6	3033
25791	1 d	,,	1598	21443	0	4077·8	3073
						4358·3	1495
24230	1	3663·3	3060				
24091	0 d	4046·6	614	21327	0	4046·6	3378
						4358·3	1611
23886	1	,,	819				
23702	2 dr	,,	1003	19882	3	4358·3	3056
23528	0	,,	1177	19549	0 v.b. (double)	,,	3389
23506	0	4077·8	1010				

TABLE XXXIX.

Glycerine



Raman lines,		Exciting lines λ. A. U.	Δν	Raman lines.		Exciting lines λ. A. U.	Δν
Wave no. in Vacuo per cm.	Intensity,			Wave no. in Vacuo per cm .	Intensity.		
23423	1	4358·3	—485	22097	1	4358·3	841
22517	0	4347·5	478	22015	1	4358·3	923
				21858	4d	4358·3	1080
22453	5	4358·3	485	21472	3	4358·3	1466
22259	0	4358·3	679	20018	4	4358·3	2920

TABLE XL

Formic acid. H.COOH.

Raman lines.		Exciting lines λ. A. U.	Δν	Raman lines.		Exciting lines λ. A. U.	Δν
Wave number in Vacuo per cm.	Intensity.			Wave number in Vacuo per cm.	Intensity.		
24430	1	3650·1	2959	22742	1 v.d.	4358·3	196
24256	0 double	4046·6	449	22246	1	,,	692
24018	1	,,	687	21886	0	,,	1052
23848	0 v.d	,,	857	21748	4 b.	4046·6	2957
23482	2	,,	1223	21540	2 b.	4358·3	1398
23301	3	,,	1404	21244	2 v.b.	,,	1694
23119	0	4077·8	1397	19981	1	,,	2957

TABLE XLI

2. Acetic acid. $CH_3.COOH$.

Raman lines.		Exciting lines λ. A.U.	Δν	Raman lines.		Exciting lines λ. A.U.	Δν.
Wave no. in Vacuo per cm.	Intensity.			Wave no. in Vacuo per cm.	Intensity.		
26773	5 d	3650·1	616	23577	0	4046·6	1128
26736	0	3654·8	618	23387	0	4077·8	1129
26623	1	3650·1	766	23331	0	4046·6	1374
26464	1	3650·1	925	23269	2b	,,	1436
26262	1	,,	1127	23110	0	4077·8	1406
26109	0 b	,,	1280	22655	0	4358·3	283
26025	0	,,	1364	22576	1	,,	362
25965	0	,,	1424	22482	1	,,	456
25714	1	,,	1675	22316	3	,,	622
24445	2	,,	2944	22041	4	,,	897
24410	2	3654·8	2944	21760	5	4046·6	2945
24270	1	4046·6	435	21705	1	4347·8	1290
24080	3	,,	625	21663	3	4358·3	1275
23802	5	,,	903	21576	3	,,	1362
23759	1	,,	946	21500	3	,,	1438
23727	1	,,	978	21271	1	,,	1665
23684	0	,,	1021	19996	1	,,	2942
23618	1	4077·8	908				

TABLE XLII

3. Propionic acid. $CH_3.CH_2.COOH$.

Raman lines.		Exciting lines λ. A.U.	Δν.	Raman lines.		Exciting lines λ. A.U.	Δν.
Wave no. in Vacuo per cm.	Intensity.			Wave no. in Vacuo per cm.	Intensity.		
26899	0b	3650·1	490	25830	0	3663·3	1460
26781	1 v.d.	,,	608	25727	1	3650·1	1662
26623	2 s	,,	766	24435	2	,,	2954
26580	0	3654·8	774	24399	2	3654·8	2955
26542	6 d	3650·1	847				
26451	1 d	3663·3	839	24226	0	4046·6	479
26255	0	3650·1	1134				
26215	0	3654·8	1139	23845	4	4046·6	860
26099	0 d	3650·1	1290				
26024	0	,,	1365	23672	0	4046·6	1033
25963	4 v.d.	,,	1426	23623	2 s.	,,	1082
25930	4 v.d.	3650·1	1459	23448	0 d.	,,	1257
		3654·8	1424	23277	3 b.	,,	1428
				23244	3 s.	,,	1461

TABLE XLIII.

4. Butyric acid. $CH_3.CH_2.CH_2.COOH$.

Raman lines.		Exciting lines λ. A.U.	Δν	Raman lines.		Exciting lines λ. A.U.	Δν
Wave no. in Vacuo per cm.	Intensity.			Wave no. in Vacuo per cm.	Intensity.		
26620	1	3650·1	769	22476	1	4358·3	462
26253	2b	,,	1136	22325	1	,,	613
25973	0	,,	1416	22126	0	4347·5	869
25935	0	,,	1454	22068	1	4358·3	870
25844	0	3663·3	1446	21951	0	4347·5	1044
25730	1	3650·1	1659	21895	1	4358·3	1043
24410	0	3654·1	2944	21824	1	,,	1114
23917	0	4046·6	788	21773	3	4046·6	2932
23837	1	,,	868	21545	1	4358·3	1293
23659	2	,,	1046	21574	1	,,	1364
23601	1	,,	1104	21485	1	,,	1453
23285	1	,,	1416	21280	1	,,	1658
23247	4	,,	1458	20055	1	4347·5	2940
22669	0	4358·3	269	19997	1	4358·3	2941

TABLE XLIV.

Acetone, $CH_3 \cdot CO \cdot CH_3$.

Raman lines.		Exciting lines λ.A.U.	Δν.	Raman lines.		Exciting lines λ.A.U.	Δν.
Wave No. in Vacuo per cm.	Intensity.			Wave No. in Vacuo per cm.	Intensity.		
27071	0	3341·5	2847	21998	0	4358·3	940
26886	0	,,	3032	21845	0	4046·6	2860
26776	0	,,	3342	...		4358·8	1093
26259	1	,,	3659	21775	10	4046·6	2930
26123	0	3650·1	1266	...			
26024	1	,,	1365	21708	2	4358·3	1230
25949	0	,,	1440	21596	1	4046·6	3109
23913	5	4046·6	792	21504	2	4358·3	1434
23714	1	3650·1	3675	21220	2	,,	1718
23625	1	4046·6	1080	21049	1	4046·6	3656
23474	2	,,	1231	20982	1	,,	3723
23280	2	,,	1425	20074	1	4358·3	2864
22578	1	4358·3	360	20012	2	,,	2926
22394	1	,,	544	19896	2	,,	3042
22140	5	,,	798	19805	1	,,	3133
				19192	1	,,	3746

TABLE XLV.

Methyl-ethyl ketone. $CH_3 \cdot CO \cdot C_2H_5$

Raman lines.		Exciting lines λ.A.U.	Δν	Raman lines.		Exciting lines. λ.A.U.	Δν.
Wave No. in Vacuo per cm.	Intensity.			Wave No. in Vacuo per cm.	Intensity.		
26825	2	3650·1	564	23327	2 b	4046·6	1378
26613	2	,,	776	23274	2	,,	1431
26265	1	3341·8	3650	22530	2	4358·3	408
26134	1	3650·1	1255	22385	2 double	,,	553
26017	2	,,	1372	22177	3	,,	761
25968	2	,,	1426	21974	0 b	,,	964
24458	2 b	,,	2931	21779	5	4046·6	2926
24141	3	4046·6	564	21731	0	4358·3	1207
23943	5	,,	762	21563	0	,,	1375
23742	2 double	4046·6	963	21500	3 b	,,	1438
		3650·1	3647	21209	2	,,	1729
23612	2	4046·6	1093	21049	1	4046·5	3656
23529	1	,,	1176	20062	2	4358·3	2876
23451	1	,,	1254	20017	4	,,	2921

TABLE XLVI.

Methyl-propyl ketone. $CH_3 \cdot CO \cdot C_3H_7$.

Raman lines.		Exciting lines λ.A.U.	Δν.	Raman lines.		Exciting lines λ.A.U.	Δν
Wave No. in Vacuo per cm.	Intensity.			Wave No. in Vacuo per cm.	Intensity.		
25673	0	3650·1	1716	21492	1	4358·3	1446
23980	0	4046·6	725	21206	1	,,	1736
22347	0	4358·3	591	20072	3 double	,,	2866
22235	0	,,	703	16596	0	5460·7	1712
21896	0	,,	1042	15400	1	,,	2908
21792	5 b	4046·6	2918				

TABLE XLVII.

Diethyl ketone. $C_2H_5.CO.C_2H_5$.

Raman lines.		Exciting lines. λ. A.U.	$\Delta\nu$	Raman lines.		Exciting lines. λ. A.U.	$\Delta\nu$
Wave No. in Vacuo per cm.	Intensity.			Wave No. in Vacuo per cm.	Intensity.		
24140	1	4046·6	565	22165	2	4358·3	773
23933	0	,,	772	21952	1	,,	986
23716	0	,,	989	21781	8	4046·6	2924
23608	1	,,	1097	21501	1 (double)	4358·3	1437
23466	1	,,	1239	21223	0	,,	1711
23294	1	,,	1411	20031	4 v.b.	,,	2907
23236	2	,,	1469	15365	1	5460·7	2943
22532	2	4358·3	406				
22381	1	,,	557				

TABLE XLVIII.

Acetophenone. $C_6H_5.CO.CH_3$.

Raman lines.		Exciting lines λ. A. U.	$\Delta\nu$	Raman lines.		Exciting lines λ. A.U.	$\Delta\nu$
Wave No. in Vacuo per cm.	Intensity.			Wave No. in Vacuo per cm.	Intensity.		
23109	2	4046·6	1596	21866	2	4358·3	1072
22776	2	4358·3	162	21779	2	,,	1159
22320	1	,,	618	21678	3	,,	1260
22212	2	,,	726	21647	2	4046·6	3058
21945	6s	,,	993	21346	8s	4358·3	1592
21921	1	,,	1017	21259	7s	,,	1679
				19884	3d	,,	3054

TABLE XLIX.

Nitromethane. $CH_3.NO_2$.

Raman lines.		Exciting lines. λ. A.U.	Δν	Raman lines.		Exciting lines λ. A. U.	Δν
Wave No. in Vacuo per cm.	Intensity.			Wave No. in Vacuo per cm.	Intensity.		
25831	0	3650·1	1558	21831	0	4358·3	1107
24219	0	4046·6	486	21741	6	4046·6	2964
24049	2	,,	656	21662	0	,,	3043
23788	5	,,	917	21542	7 dv	4358·3	1396
23591	2	,,	1114	21376	1	,,	1562
23308	5 b. dv	,,	1397	19978	3	,,	2960
23141	0d	,,	1564	19897	0	,,	3041
22454	8b	4358·3	484				
22284	5	,,	654	15348	1	5460·7	2960
22023	8	,,	915				

TABLE L.

Tetranitromethane. $O_2N—C(NO_2)_3$

Raman lines.		Exciting line. λ. A.U.	Δν
Wave No. in Vacuo per cm.	Intensity.		
16977	1	5460·7	1331

TABLE LI.

Nitro-benzene. $C_6H_5NO_2$.

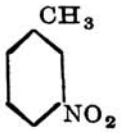
Raman lines.		Exciting lines. λ. A.U.	Δν	Raman lines.		Exciting lines. λ. A.U.	Δν
Wave No. in Vacuo per cm.	Intensity.			Wave No. in Vacuo per cm.	Intensity.		
22077	1	4358·3	861				
21927	2	,,	1011				
21822	2	,,	1116	16962	7	5460·7	1346
21647	0	4347·5	1348	16711	2	,,	1597
21590	8	4358·3	1348	16254	0	5790·7.	1010
21407	0	,,	1531	15983	1	5769·6	1344
21356	3	,,	1582	15910	0	5790·7	1354
19893	0	,,	3045	15233	1	5460·7	3075

TABLE LII.

Ortho-nitrotoluene

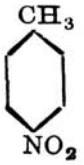
Raman lines		Exciting lines λ. A.U.	Δν	Raman lines.		Exciting lines λ. A.U.	Δν
Wave No. in vacuo per cm.	Intensity.			Wave No. in vacuo per cm.	Intensity.		
21897	2	4358·3	1041				
21749	1b	,,	1189				
21598	6	4046·6	3112	17519	1	5460·7	789
...	...	4358·3	1345	16977	8	,,	1331
21464	0	4358·3	1474	16736	2d	,,	1572
21348	2	,,	1590	15355	1	,,	2953
19889	1	,,	3049	15221	1	,,	3087

TABLE LIII.

Meta-nitrotoluene 

Raman lines.		Exciting line λ. A. U.	Δν
Wave No. in vacuo per cm.	Intensity.		
16982	2	5460·7	1326

TABLE LIV.

Para-nitrotoluene 

The crystals were dissolved in carbon tetrachloride and the spectrum of the solution was taken. The CCl_4 lines are omitted in the following table.

Raman lines.		Exciting lines λ. A. U.	Δν
Wave No. in vacuo per cm.	Intensity		
21593	4	4358·3	1345
21348	0	,,	1590
16982	1	5460·7	1326

TABLE LV.

Benzene* C_6H_6.

Raman lines		Exciting line λ. A.U.	Δν	Raman lines		Exciting lines. λ. A.U.	Δν
Wave No. in vacuo per cm	Intensity.			Wave No. in vacuo per cm	Intensity.		
26782	2	3650·1	607	23715	10	4046·6	990
26747	1	3654·8	607	23541	0	4358·3	—603
26683	0	3663·3	607	23529	5	4077·8	987
26534	0	3650·1	855	...	...	4046·6	1176
26399	10	,,	990	23346	0	4108·9	985
26216 Imperfectly resolved	2	,,	1173	22333	1	4358·3	605
26199	2	3654·8	1155	22089	0	4358·3	849
26116	0	3663·3	1174	22004	0	4347·5	991
25797	1v.b	3650·1	1592	21948	10	4358·3	990
25698	1	4046·6	—988	21763	2	,,	1175
24294	3	3654·8	3060	21646	10	4046·6	3059
24285	4	3663·3	3055	21458	1	4077·8	3058
24103	1	4046·6	602	21348	1v.b.	4358·3	1590
23927	0	4358·3	—989	19877	1	,,	3061
23856	0	4046·6	849	...	...	...	...

* Values obtained by Mr. K. S. Krishnan

TABLE LVI.

Toluene. 

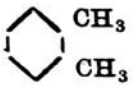
Raman lines		Exciting line λ. A.U.	Δν	Raman lines		Exciting line λ. A.U.	Δν
Wave No. in vacuo per cm	Intensity.			Wave No. in vacuo per cm	Intensity		
26869	1	3650·1	520	23676	1	4046·6	1 029
26828	0	3654·8	526	23553	0	,,	1152
26772	1	3650·1	617	23500	1	,,	1205
26728	0	3654·8	626	23455	0	4358·3	—517
26604	1	3650·1	785	23326	0	4046·6	1379
26570	0	3654·8	784	23165	0	4358·3	—227
26357	1	3650·1	1032	23104	0	4046·6	1601
26266	0	3663·3	1024	22723	1	4358·3	215
26235	0	3650·1	1154	22593	1	,,	345
26013	0	,,	1376	22474	0	4347·5	521
25969	0	,,	1420	22419	2	4358·3	519
25785	1	,,	1604	22316	1	,,	622
25747	0	3654·8	1607	22208	0	4347·5	787
24468	1	3650·1	2921		...	4358·3	730
24438	0	3654·8	2916	22153	2	4358·3	785
24370	1	3663·3	2920	21986	0	4347·5	1009
				21933	2	4358·3	1005
		4046·6	335	21909	1	,,	1029
24292	1	3654·8	3062	21776	1b.	4046·6	2929
24243	1	3663·3	3047		...	4358·3	1162
24185	1	4046·6	520	21729	1	4358·3	1209
24087	I	4046·6	618	21648	1 dv.	4046·6	3057
23939	0	4358·3	—1001	21555	0	4358·3	1383
23922	1	4046·6	783	21507	0	,,	1431
23725	0	4358·3	—787	21435	0	,,	1503
23705	2	4046·6	1000	21336	1	,,	1602
				20017	0	,,	2921
				19886	1	,,	3052

TABLE LVII.

Ethyl benzene $CH_3\text{-}CH_2$

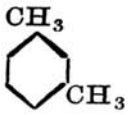
Raman lines.		Exciting line. λ. A. U.	Δν	Raman lines.		Exciting line. λ. A. U.	Δν
Wave numbers in vacuo per cm.	Intensity.			Wave Nos. in vacuo per cm.	Intensity.		
27006	2	3341·5	2912	23732	0	4046·6	978
26772	0	3650·1	617	23704	2s	,,	1001
26624	1	,,	765	23679	0	,,	1026
26427	0	,,	962	23552	0	,,	1153
26352	2	,,	1037	23505	2	,,	1200
		3654·8	1002	23249	0	,,	1456
26323	0	,,	1031	23097	0	,,	1608
26265	0 broad	3663·3	1025	22785	4 v. b	4358·3	153?
				22633	0	,,	305
				22539	0	,,	399
25938	0	3650·1	1451	22491	0	,,	447
25784	1broad	,,	1605	22313	0	,,	625
25745	0	3654·8	1609	22168	2 v. b	,,	770
25675	0	3663·3	1615	21967	0	,,	971
				21931	2s	,,	1007
				21904	0	,,	1034
				21767	2	4046·6	2938
24454	0	3650·1	2935	21733	2	4358·3	1205
24421	0	3654·8	2933	21648	4 b	4046·6	3057
24380	0	3663·3	2910	21478	1double	4358·3	1460
24292	0	3654·8	3062	21331	2 b	,,	1607
24286	1	4046·6	469	20 007	2 b (double)	,,	2939
24166	0	,,	539	19886	8	,,	3052
24087	1	,,	618				
23986	2	,,	770	17544	0	5460·7	764
23901	0	4077·8	615	16714	0	,,	1594

TABLE LVIII.

Ortho-xylene 

Raman lines.		Exciting line. λ. A. U.	Δν	Raman lines.		Exciting line. λ. A. U.	Δν
Wave numbers in vacuo per cm.	Intensity.			Wave Nos. in vacuo per cm.	Intensity.		
23975	2	4046·6	730	21937	1	4358·3	1001
23889	0	,,	816	21837	0	4046·6	2868
23788	0	4077·8	728	21782	2d	,,	2923
23709	1	4046·6	996	21637	1d	,,	3068
23651	0	,,	1054	21485	0	4358·3	1453
23466	0	4077·8 4046·6	1050 1239	21334	0	,,	1604
23247	0	4046·6	1458				
22952	0	4358·3	586				
22322	0	4358·3	616(?)	20069	2	,,	2869
				20016	2 d	,,	2922
22287	0	,,	651				
22213	2	,,	725	19888	2	,,	3050
22037	0	4339·2	1002	15393	0 d	5460·7	2915

TABLE LIX.

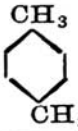
Meta-xylene 

Raman lines.		Exciting line. λ. A. U.	Δν	Raman lines.		Exciting line. λ. A. U.	Δν
Wave numbers in vacuo per cm.	Intensity.			Wave Nos. in vacuo per cm.	Intensity.		
27119	0 d	3650·1	270	23260	0	4077·8	1256
27075	0	3341·5	2843	23090	0	4046·6	1615
26655	3	3650·1	734	22724	1	4358·3	214
26566	0dv	3663·3	724	22667	0	,,	271
26381	3	3650·1	1008	22407	1	,,	531
26223	0	,,	1166	22209	2	,,	729
26011	0 (double)	,,	1378	21397	2	,,	1001
24473	0 broad	,,	2916	21842	0	4046·6	2863
24424	0 ,,	4046·6	281	21784	2 broad	,,	2921
24374	0 ,	3650·1	3015			4358·3	1154
24241	0 ,,	4046·6	464	21685		,,	1253
24175	1d	,,	530	21669	2*	4046·6	3036
23978	2	,,	727	21653		4358·3	1285
				21564	0	,,	1374
23778	0	4077·8	738	21476	0 d	,,	1462
23707	2	4046·6	998	21333	1 d	,,	1605
23522	0 broad	,,	1180	20103	0 broad	4339·2	2892
		4077·8	994	20065	1	4358·3	2873
23447	1 broad	4046·6	1258	20030	0	,	2908
23331	1	,,	1374	19901	0	,,	3037

* Not well resolved.

TABLE LX.

Para-xylene



Raman lines.		Exciting line λ. A.U.	Δν.	Raman lines.		Exciting line λ. A.U.	Δν.
Wave numbers in vacuo per cm.	Intensity.			Wave numbers in vacuo per cm.	Intensity.		
27077	0	3650·1	312	23876	5	4046·6	829
27035	0	3654·8	319	23696	0	,,	1009
						4077·8	820
26929	0	3650·1	460	23500	6	4046·6	1205
26894	0	3654·8	460	23453	0	,,	1252
26785	0	3341·5	3133	23409	1	,,	1296
26748	0	3650·1	641	23327	2 broad	,,	1378
26696	0	,,	693	23249	1 ,,	,,	1456
26561	1	,,	828	23088	1	,,	1617
26429	0	,,	960	22623	2	4358·3	315
				22545	0	,,	393
26232	0	,,	1157	22477	2	,,	461
26180	3	,,	1209	22294	2	,,	644
26145	1	,,	1244	22111	6	,,	827
26087	1	,,	1302	21966	0	,,	972
26010	1	,,	1379	21832	2	,,	1106?
						4046·6	2873
25981	0	3654·8	1373	21780	5	4046·6	2925
						4358·3	1158
				21729	3 sharp	,,	1209
25769	2	3650·1	1620	21689	3	4358·3	1249
25733	0	3654·8	1621	21647	4	4358·3	1291
						4046·6	3058
24465	0	3650·1	2924	21562	2	4358·3	1376
24377	0*	,,	3017	21476	1	,,	1462
		4046·6	328	21324	3	,,	1614
24245	2	,,	460				
24163	0	,,	542				
24057	2	,,	648	20073	0	,,	2865
24017	0	,,	694	20018	2	,,	2920
23921	0	,,	784	19897	1 d	,,	3041

* Very broad; probably double.

TABLE LXI.

Ethyl ether $C_2H_5-O-C_2H_5$.

Raman lines.		Exciting line λ. A.U.	Δν.	Raman lines.		Exciting line λ. A.U.	Δν.
Wave numbers in vacuo per cm.	Intensity.			Wave numbers in vacuo per cm.	Intensity.		
24453	4*d*	3650·1	2936	22142	0	4358·3	796
24415	4*d*	,,	2974	22092	3*d*	,,	846
24363	2*d*	,,	3026	22012	2*d*	,,	926
24260	2*d*	4046·6 3650·1	439 3123	21895	3*d*	,,	1043 double.
23906	0	4046·6	799	21832	6*d*	4046·6	2873
23862	3	,,	843	21768	6*d*	,,	2937
23775	1*d*	,,	930	21723	6*d*	,,	2982
23678	1	,,	1027	21660	2 very broad.	4358·3	1278
23623	0	,,	1082	21581	2*d*	4339	1458
23555	1	,,	1150	21530	2*d*	4077·8 4347·5	2986 1465
23508	0	,,	1197	21483	5 broad	4358·3	1455 double.
23442	1	,,	1263	20069	4*d*	,,	2869
23371	1	,,	1334	20004	4*d*	,,	2934
23246	2 very broad.	,,	1459 double.	19962	4*d*	,,	2976
22496	3*s*	4358·3	442				

TABLE LXII.

Phenyl methyl ether C_6H_5-O-CH_3.

Raman lines.		Exciting line λ. A.U.	Δν.	Raman lines.		Exciting line λ. A.U.	Δν
Wave numbers in vacuo per cm.	Intensity.			Wave numbers in vacuo per cm.	Intensity.		
23924	1	4046·6	781	21890	0	4046·6	2815
23707	2	,,	998	21764	1	4358·3 4046·6	1174 2941
23543	0	,,	1162	21704	0	4358·3	1234
22497	0	4358·3	441	21641	3	4046·6	3064
22311	0	,,	627	21497	1 v.d.	4358·3	1441
22152	1	,,	786	21354	1	,,	1584
21937	3	,,	1001	19897	1 d.	,,	3041

TABLE LXIII.

Cyclohexane C_6H_{12}.

Raman lines.		Exciting line λ. A.U.	Δν	Raman lines.		Exciting line λ. A.U.	Δν
Wave No. in vacuo per cm.	Intensity.			Wave No. in vacuo per cm.	Intensity.		
24536	2	3650·1	2853	22832	0	4358·3	606
24467	2	,,	2922	22239	0	4339·2	600
24454	2	,,	2935	22193	1	4347·5	802
24436	2	3663·3	2854	22138	4 s	4358·3	800
24419	2	3654·8	2935	22042	1	4339·2	997
24370	2	3663·3	2920	22009	0	4347·5	986
24353	2 d	,,	2935	21946	2 s	4358·3	992
24323	0	4046·6	382	21911	2	,,	1027
24289	0 double	,,	416	21852	4	4046·6	2853
24227	1	,,	478	21815	1 b	,,	2890
24096	0	,,	609	21784	3	,,	2921
23904	4	,,	801	21768	3	,,	2937
23738	0	4358·3	—800			4358·3	1170
23712	3 s	4046·6	993	21669	3	4358·3	1269
		4077·6	800	21662	1	4077·8	2856
23677	2 b	4046·6	1028	21628	2	,,	2888
23548	1	,,	1157	21595	2	,,	2921
23522	1	4077·8	994			4358·3	1848
23488	0	,,	1028	21580	2	4077·8	2936
23438	2	4046·6	1267			4339·2	1489
23357	1	,,	1348	21492	3	4366·3	1446
23261	2 d	,,	1444	20090	3	,,	2848
22555	0	4358·3	383	20008	3 b	,,	2930
22513	0	,,	425				

TABLE LXIV.

Pyridine C_5H_5N.

Raman lines.		Exciting line λ. A.U.	Δν	Raman lines.		Exciting lines λ. A.U.	Δν
Wave No. in vacuo per cm.	Intensity.			Wave No. in vacuo per cm.	Intensity.		
26785	1	3650·1	604	23487	4	4046·6	1218
26739	2	,,	650			4077·8	1029
26700	1	3654·8	654	23301	0	4077·8	1215
26402	10	3650·1	987	23219	0	4046·6	1486
26366	10	,,	1023	23131	1	,,	1574
		3654·8	988	22533	1	4358·3	405
26327	3	,,	1027	22335	1	,,	603
26263	5	3663·3	1027	22288	3	,,	650
26135	0	3654·8	1219	22053	1	4339·2	986
26074	1	3663·3	1216			4358·3	885
26018	0	3650·1	1371	22005	1	4347·5	990
25814	2	,,	1575			4358·3	933
25779	0	3654·8	1575	21950	5	4358·3	988
25715	0	3663·3	1575	21909	5	,,	1029
24295	2	3654·8	3059	21781	2	,,	1157
24236	4	3663·3	3054	21718	2	,,	1220
24102	1	4046·6	603	21652	10	4046·6	3053
24054	3	,,	651	21556	1	4358·3	1382
23819	1	,,	886	21461	3	,,	1477
23768	0	,,	937			4077·8	3055
23716	10	,,	989	21358	3	4358·3	1590
23675	10	,,	1028	19885	4	,,	3053
23528	1	4077·8	988				

TABLE LXV.

Nitric acid, HNO_3

Raman lines.		Exciting line. λ. A.U.	Δν	Raman lines.		Exciting line. λ. A.U.	Δν
Wave No. in vacuo per cm.	Intensity.			Wave No. in vacuo per cm.	Intensity.		
26701	0	3650·1	688	23470	0	4077·8	1046
26445	0	,,	944	23395	3 b	4046·6	1310
26344	3 b	,,	1045	22477	0	4358·3	461
26251	2 b	,,	1138	22299	2	,,	639
26086	1 b	,,	1303	22243	2	,,	695
25990	0 b	3663·3	1300	21985	3	,,	953
24241	0	4046·6	464	21893	5s	,,	1045
24068	2	,,	637	21818	0	,,	1120
24017	2	,,	688	21635	4	,,	1303
23746	3 b	,,	959	21517	1 b	4046·6	3188*
23658	5	,,	1047	21285	2 b	,,	3420*
23573	0 b	,,	1132	21156	2 b	,,	3549*

* Water bands.

TABLE LXVI.

Sulphuric acid H_2SO_4

Raman lines.		Exciting line. λ. A.U.	$\Delta\nu$	Raman lines.		Exciting line. λ. A.U.	$\Delta\nu$
Wave No. in vacuo per cm.	Intensity.			Wave No. in vacuo per cm.	Intensity.		
26811	2	3650·1	578	22521	2	4046·6	2184
26716	1	3663·3	574	22377	4 b	4358·3	561
26471	2	2650·1	918	22078	0	4347·5	917
24140	3 b	4046·6	567	22029	3 b	4358·3	909
23797	3 b	,,	908	21895	1	,,	1043
23659	2	,,	1046	21783	1	,,	1155
23562	0	,,	1143	20893	0	,,	2045
23366	0	,,	1339	20765	0	,,	2173
22664	0	,,	2041	20566	0	,,	2372